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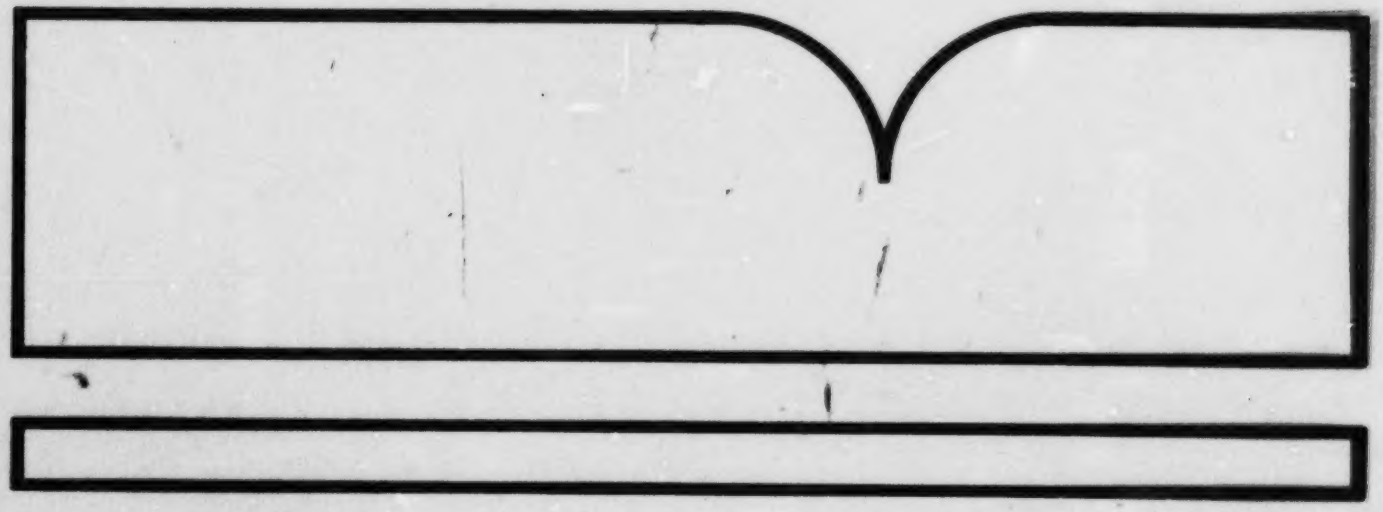

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ALTERNATIVE WATER DISINFECTION SCHEMES FOR REDUCED TRIHALOMETHANE FORMATION

Volume I. Prototype Studies

by

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16. ABSTRACT

The primary objective of this study was to develop techniques to reduce or eliminate THM in finished water without compromising the microbiological quality of the water. To this end a prototype rapid mixing system was employed and a number of alternative disinfection systems investigated. From these data both a general predictive model was developed and the role of algae and humic acids as THM precursors was evaluated.

Results of this study support the contention that in disinfection practice a tubular plug flow reactor can be used to advantage in reducing bacterial populations in the water. An added advantage is that use of this type reactor will result in minimal THM formation with chlorine as the disinfectant.

Through seeded experiments, it was shown that the disinfection systems of chlorine, chlorination followed by ammonia, and chlorine dioxide were very effective when used with hydraulic mixing. Chlorine dioxide was shown to be the better disinfectant under the conditions of this study.

Of greater importance was the substantial reduction in THM production observed with the prototype system. The lower chlorine doses required for effective disinfection resulted in significantly lower THM production. The two best systems for minimizng THM production were chlorine dioxide and ammonia plus chlorine.

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Disinfectants Ammonia Bacteriophage Chlorine Chlorophyll Disinfection Escherichia coli Humic acids Models	Chloramine Chlorine dioxide Hydraulic mixing Precursors Standard plate count Trihalomethanes	13B

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FORWORD

The U. S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This study was designed to evaluate alternative disinfection systems for the reduction of trihalomethanes in finished waters. A rapid mixing scheme was employed to optimize disinfection while minimizing trihalomethane formation. Reductions in trihalomethane formation as high as 295-fold were achieved in this study without severely compromising the microbiological quality of the treated water.

Francis T. Mayo, Director
Municipal Environmental Research
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ABSTRACT

The potential adverse health effects of organohalides, particularly trihalomethanes, in drinking water are of serious national concern. Trihalomethanes (THM) are formed primarily by the reaction between organic precursors in the water and chlorine, the halide most widely used for disinfection of potable water.

The primary objective of this study was to develop techniques to reduce or eliminate THM in finished water without compromising the microbiological quality of the water. To this end, a prototype rapid mixing system was employed, and a number of alternative disinfection systems were investigated. From these data, both a general predictive model was developed and the role of algae and humic acids as THM precursors was determined.

Results of this study support the contention that in disinfection practice, a tubular plug flow reactor can be used to advantage in reducing bacterial populations in the water. An added advantage is that use of this type of reactor will result in minimal THM formation with chlorine as the disinfectant.

Through seeded experiments, it was shown that the disinfection systems of chlorine chlorination followed by ammonia and chlorine dioxide were very effective when used with hydraulic mixing. Chlorine dioxide was shown to be the better disinfectant under the conditions of this study.

Of greater importance was the substantial reduction in THM production observed with the prototype system. The lower chlorine doses required for effective disinfection resulted in significantly lower THM production. The two best systems for minimizing THM production were chlorine dioxide and ammonia plus chlorine. Specifically, a 17-fold reduction in THM production was observed at a 1.5 mg/l chloramine dose when compared with the same dose of chlorine alone. A 275-fold reduction in THM production was observed under the same conditions for ammonia followed by chlorine.

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ABBREVIATIONS AND SYMBOLS

ac ft	acre feet
b	regression coefficient(s)
C	centrigrade scale
ca.	approximately
cfu	colony forming units
CLN	chlorine followed by ammonia
cm	centimeters
cu yd	cubic yards
°	degree
FAC	free available chlorine
ft	feet
gal	gallons
gal/min	gallons per minute
hr	hours
in	inches
Inst THM	instantaneous trihalomethane(s)
K	kelvin scale
km	kilometer
l	liter
l/s	liter per second
m	molar; meter
M	number of contact intervals
m^3/day	cubic meter per day
mgd	million gallons per day
µg/l	micrograms per liter
mg/kg/day	milligrams per kilogram of body weight per day
mg/l	milligrams per liter
ml	milliliters
mm	millimeters
pfu	plaque forming units
r	disinfectant residual, mg/l
R	universal gas constant (1.987 calories /°K); disinfectant residual
R_i	free chlorine residual at end of contact interval, mg/l
rpm	revolutions per minute
S	survival ratio
sec	seconds
SPC	standard plate count
sq in	square inches
sq mi	square miles
t	contact time in seconds
T	temperature, °K
TAC	total available chlorine
Term THM	terminal trihalomethane(s)
THM	trihalomethane(s)
TTHM	total trihalomethane(s)
THMFP	trihalomethane formation potential
t_i	contact interval, sec
TOC	total organic carbon
WTP	water treatment plant
y	survival fraction of SPC organisms
Z	THM concentration, µg/l

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SECTION 1

INTRODUCTION

The use of chlorine as a disinfectant in potable water has been based on its long and successful history of rendering water sufficiently free of pathogenic organisms, thereby minimizing the probability of waterborne disease among the consuming public. Because of its relative ease of application and low cost, chlorination has become synonymous for disinfection. The widespread use of chlorine has been one of the most important public health control measures of this century. Recently, potential adverse health effects have been linked to organohalides, particularly trihalomethanes (THM), in drinking water. These organohalides are formed primarily by the reaction between organic precursors in the water and the chlorine disinfectant introduced into the water stream.

The primary objective of this investigation was to develop techniques to reduce or eliminate THM and other organochlorine compounds in finished water without compromising the microbiological quality of the water. To accomplish this goal, a rapid mixing system employing a plug flow reactor was examined with several disinfectants. The THM produced and the disinfection efficiency of alternative disinfectant schemes were compared with chlorine. The alternate disinfectant schemes used were chlorine dioxide, ammonia followed by the addition of chlorine (chloramine), and chlorine followed by the addition of ammonia. The original scope of the investigation was altered by the addition of chloramine as a test disinfectant and the deletion of chlorine with chlorine dioxide as disinfectants.

The second objective was to develop a general predictive model for process control. The model was to address the efficacy and economy of the disinfectants studied in relation to maximizing disinfection efficiency and minimizing THM production.

The third objective was to evaluate the role of algal cells (including chlorophyll-a), algal extracellular metabolites, and humic acids present in the source water as THM precursors.

SECTION 2

CONCLUSIONS

1. Chlorine dioxide is a much better disinfectant than chlorine for standard plate count (SPC) organisms in the rapid mixing system.

2. For contact times greater than one hour, the chloramination disinfection system (chlorine followed by the addition of ammonia), proved to be a better disinfection system for SPC organisms when compared to the chlorine dioxide and chlorine disinfection systems on a gravimetric basis.

3. Bacteriophage f_2 was effectively inactivated with chlorine under the rapid mixing conditions employed.

4. Highly turbulent mixing of chlorine followed by ammonia addition resulted in reduced THM levels (10-20 µg/l with trihalomethane formation potential of approximately 130 µg/l) with effective SPC organism reduction.

5. The prototype mixing system effectively reduces THM initially and maximizes disinfection. Prolonged contact with the disinfecting agent, chlorine, produces additional THM if a free residual persists.

6. Soluble humic materials may be responsible for a significant portion of THM formation potential in the Boerne reservoir water.

7. Chlorophyll-a is responsible for a small but real portion of THM formation potential in the Boerne reservoir water.

SECTION 3

RECOMMENDATIONS

1. The chlorine, chloramination and chlorine dioxide disinfection systems evaluated for bacterial disinfection efficiency in this study should be further evaluated for virus disinfection efficiency.

2. Evaluation of the effects of mixing on inactivation of virus with different disinfectant systems is required.

3. Evaluation of specific mixing parameters is required to determine the appropriate geometry and energy input parameters applicable to engineering design of the mixing system to allow design of a cost effective mixing system.

4. Isolation of endogenous organic materials in raw reservoir water and the examination of their THM formation potentials is needed.

5. Evaluation of the effect of higher added doses of chlorophyll-a on the production of THM is necessary.

SECTION 4

LITERATURE REVIEW

CHLOROORGANICS IN WATER

Recently, increased attention has been focused on organic substances in potable water supplies. Since the discovery of the production of haloforms and organochlorine compounds during the chlorination of natural waters, efforts have been made to identify the precursor compounds and control the amounts of organohalides produced. The most notable chlorinated organic compound which has been found is chloroform.

Considering the widespread use of chlorine in drinking water treatment, a significant health hazard may be associated with high levels of chloroform and/or other chloroorganics. Chloroorganics have been implicated by Harris and Page (1974) as annually causing over 50 premature cancer deaths among New Orleans' white male population. Although chloroform is not listed by the National Academy of Sciences in a recent report (National Archives of the United States, July, 1977) to the Environmental Protection Agency as a known or suspected human carcinogen, its effects have been examined in three animal species utilizing two routes of exposure. In five studies a tumorigenic response was demonstrated while in four others no tumors were detected (Tardiff, 1977).

Stokinger (1977) has suggested that the levels of chloroform present in drinking water cannot present a significant health hazard primarily because extrapolating cancer incidence from animal data to man can be fallacious.

However, Tardiff (1977), taking the alternative position has estimated that if drinking water doses are 0.01 mg/kg/day, chloroform in water may be responsible for as much as 1.6% of the current yearly human liver cancer incidence in the United States and for as much as 1.44% of the yearly kidney cancer. Furthermore, Commoner (1977) has suggested that 75% - 80% of cancer incidence is of environmental origin, and he believes that the majority of known carcinogens are synthetically produced organic chemicals.

A maximum contaminant level of 0.1 mg/l total THM has been established by the United States Environmental Protection Agency for systems serving populations of greater than 10,000 persons (Federal Register, 1979). However, it has been pointed out that health risk assessments would be better based on the total number of carbon-chlorine bonds rather than on the extent of chloroform or haloform formation only (Morris and Baum, 1978). This recommendation was made because most halogenated compounds (volatile and nonvolatile) formed by chlorination are likely to show possible carcinogenic risks.

The ubiquitous nature of THM precursors necessitates the development of techniques and methods to reduce THM and other organochlorine concentrations in finished waters. Nevertheless, it may be necessary to tolerate threshold levels of chloroorganic contaminants if alternative modes of disinfection are unacceptable. Techniques likely to reduce the concentration of chloroform and other THM also are likely to reduce the concentrations of other chlorinated organic compounds. Approaches to control organochlorine production include: utilization of alternative disinfectants, control of the THM formation potential, and reduction of the THM concentration after formation.

To accomplish the reduction of THM in an economical manner, an expanded knowledge of the factors that influence total trihalomethane (TTHM) production are needed on both the laboratory and water treatment plant scale. Pioneering studies by Rook (1974) and Bellar, et al. (1974), have demonstrated that there is a definite increase in the concentration of chloroorganics in the form of THM as water passes through various treatment stages in municipal water systems. When chlorine was used to bleach natural waters, the subsequent production of THM led Rook (1974) to postulate that humic substances present were precursors for THM production. Alternatively, Bellar et al. (1974), proposed that oxidation of ethanol to acetaldehyde provided a route to THM production. Acetone and other simple ketones also have been implicated as possible precursors in THM formation (Stevens et al., 1976a). However, such precursors are not likely to be found except in wastewaters or water supplies that contain some industrial waste. A reservoir fed by runoff in a nonindustrial region would not be expected to have any significant amounts of such precursors.

Humic substances, composed primarily of humic and fluvic acids, are derived from the decomposition of plant materials and are ubiquitous in surface waters. Humic and fluvic acids are thought to be complex polymers of polyhydroxybenzenes, polyhydroxybenzoic acids, sugars, and nitrogen bases whose molecular weights range into the millions. Upon degradation both humic and fluvic acids produce similar products such as resorcinol, pyrogallol, catechol, 2, 6-dihydroxytoluene, phthalic acids, and 3, 5-dihydroxybenzoic acids. These products can be chlorinated to produce THM as well as other types of chloroorganic compounds. Rook (1976,1977) has established that haloforms are produced from both natural waters which contain humic materials and from model systems which contain chemically similar organic compounds. A natural water sample of pH 7.6 - 7.8 having a total organic carbon (TOC) content of 3.6 mg/l and six color units (platinum-cobalt scale), after exposure to a chlorine dose of 5 mg/l for one hr at 12°C, contained 37.5 µg/l of chloroform (Rook, 1976). Haloform production was demonstrated to be dependent upon pH, chlorine dose, chlorine contact time, and concentration of humic material. Model compounds such as phlorizin and 1, 3-dihydroxybenzene produced high levels of chloroform (90% - 94% and 85% - 100%, respectively) depending upon the reaction conditions (Rook, 1977). Using mass spectroscopy Rook (1977) also identified a large number of chlorinated compounds other than THM.

An additional precursor candidate for the production of THM was suggested by Hoehn et al. (1977a,b). Seasonal variations in the concentrations of THM, which correlated with runoff from a watershed, were observed. A two year study of the Occoquan Reservoir (Fairfax County, Virginia) showed improved

water quality the second year as well as a shift in the time of year when maximal THM was produced. Hoehn et al. (1977a), were able to establish a definite relationship between algae growth (measured by chlorophyll-a) and THM formation for the two year period in the reservoir. Furthermore, Hoehn et al. (1977b), have shown in laboratory studies that several types of algae as a precursor produce THM. Similar results have been observed by Morris and Baum (1977).

Thus, several operational mechanisms may result in the production of THM as a result of chlorination of natural waters. Chlorination of humic acids provides a background production of THM and during periods of intense algae bloom additional THM can be obtained from either extracellular products of algae growth or the presence of significant concentrations of chlorophyll-a. Additional studies are needed to establish if these tentative correlations are valid and important for control of THM production.

The problem of organics in drinking water and, in particular, THM in microgram per liter quantities has been stated clearly in the National Organics Reconnaissance Survey (NORS) (Symons et al., 1975) conducted by EPA in 1974-1975. In the initial study, 79 of 80 cities showed evidence of THM. Subsequently a study of 83 cities in EPA's Region V confirmed the earlier findings (Symons, 1976). Ranges of chloroform concentration from 0.1 µg/l to 366 µg/l were found (Symons et al., 1975 and Symons, 1976). The trihalomethanes present in finished water are most commonly chloroform, bromodichloromethane, dibromochloromethane, and bromoform (Symons, 1976). However carbon tetrachloride, 1, 2-dichloroethane, methylene chloride, and dichloroiodomethane also are found. With the exception of dichloroiodomethane the other three compounds are not apparently formed during chlorination (Symons, 1976).

The Interim Treatment Guide prepared by EPA addressed the problem of reducing THM concentrations in finished water (Symons, 1976). Four approaches exist for the control of THM:

1. Change disinfectant to one that does not produce THM upon disinfection.

2. Apply chlorine downstream of a process designed to remove substantial amounts of the THM precursor(s).

3. Reduce the THM concentration after its formation.

4. Change the process (i.e., better pH control) to minimize THM formation and optimize precursor removal.

Alternative disinfectants such as ozone, chlorine dioxide and chloramine do not produce measurable quantities of trihalomethanes; however, there are disadvantages to each disinfectant (Symons, 1976). The largest problem associated with use of any disinfectant, including chlorine, is the lack of data concerning the by-products formed during the disinfection process. The toxicity and/or carcinogenicity of organic by-products may represent a significant health hazard. Furthermore, the disinfectants ideally should

leave a residual for controlling aftergrowth in the distribution system as well as being initially effective in destroying waterborne viruses and bacteria.

Control of the THM concentration by removal of precursors or by removal of the THM after disinfection is a feasible approach using granular activated carbon (GAC) with or without aeration (Symons, 1976). Both precursors and THM are removed by GAC treatment as well as many other organics; however, the optimal performance lifetime of the GAC filter is limited (Symons, 1976). Alternative methods of THM reduction may provide better and less expensive solutions to the problem of chloroorganics in drinking water.

Recent advances in the techniques available for detection and identification of increasingly smaller amounts of THM and chloroorganics will allow the study of a reservoir system that will not have significant quantities of organic precursors other than naturally occurring humic and algal materials. The volatile THM can be examined by a head-gas technique using gas chromotographic analysis (Bellar and Lichtenberg, 1974) with mass spectroscopy for component identification (Lingg et al., 1977 and Kuo et al., 1977). Liquid-liquid extraction techniques also can be employed to analyze for possible precursors as well as products of the disinfection process when different disinfectants and addition modes are employed (Richard and Junk, 1977; Mieure, 1977). Therefore techniques are available to adequately measure low concentrations of THM. The determination of instantaneous THM (InstTHM), terminal THM (Term THM) and the trihalomethane formation potential (THMFP) provide a measurement of the success of efforts to remove or reduce THM produced by modified water-treatment practices (Stevens and Symons, 1977).

CHLORINE AND CHLORAMINES AS DISINFECTANTS IN WATER

In reviewing and extending the work of Shilov and Soludushenkov (1936), Morris (1946) noted that the hydrolysis of chlorine is very rapid. For all practical purposes the reaction is complete in less than one sec at 1°C. Shilov and Solodushenkov (1936) and Morris and Weil (1950) interpreted the hydrolysis reaction in terms of the following "classical" chlorine hydrolysis equation for which hydrolysis constants are listed in Table 1:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

The forward rate constant for this reaction was 4.48×10^4 sec^{-1} at 25°C. Morris (1946) interpreted the data as indicating that the reaction occurs at almost every collision. Later Connick and Chia (1959) used conductivity techniques to determine the hydrolysis rate constant. Their work was based upon the assumption that the pathway indicated by the preceding "classical" chlorine hydrolysis equation was valid.

Hypochlorous acid in aqueous solution undergoes ionization and establishes an equilibrium with hypochlorite ion as follows (Sawyer and McCarty, 1967; Palin, 1973):

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

TABLE 1. Chlorine Hydrolysis Constants
(from Connick and Chia, 1959)

Temperature °C	Hydrolysis Constant ($k \times 10^4$ sec^{-1})		
	Connick & Chia Study	Other Studies Sited	
		Range	Number of Observations
0	1.46	1.23 - 1.6	5
15	2.81	2.88 - 3.28	3
25	3.94	2.09 - 4.84	8
35	5.10	5.68 - 6.43	2
45	6.05	7.84	1

The equilibrium constant at 20°C is 2.7×10^{-8}. At pH 7.4 approximately equal concentrations of hypochlorous acid and hypochlorite ion are present, with hypochlorous acid becoming more predominant at lower pH values. Significant amounts of molecular chlorine exist at less than pH 4.

The significance of the foregoing discussion centers on the factors which influence the presence of hypochlorous acid, the most effective biocidal chlorine species. Furthermore, hypochlorous acid reacts readily with a large number of organic and inorganic materials which may be found in waters. Probably some of the most significant of these reactions are those that occur between chlorine and compounds containing nitrogen. While chloramines do not react with precursors to form trihalomethanes, they are inferior to free chlorine (hypochlorous acid plus hypochlorite ion) as a water disinfectant.

The initial reaction in the chloramine series (Morris and Weil, 1950; Morris, 1967) is the reaction between chlorine and ammonia to produce monochloramine which is expressed as

$$NH_3 + HOCl \xrightarrow{k_1} NH_2Cl + H_2O \qquad (3)$$

where the general expression for the second order rate constant is expessed as

$$k_1 = 9.7 \times 10^8 e^{-(3000/RT)} \qquad (4)$$

where:

k_1 = rate constant, liter/mol-sec

R = universal gas constant (1.987 calories/^oK)

T = temperature, ^oK

The next reaction, the formation of dichloramine, is expressed as

$$NH_2Cl + HOCl \xrightarrow{k_2} NHCl_2 + H_2O \qquad (5)$$

Reportedly, acetic acid and H_3O^+ can catalyze this reaction (Morris and Weil, 1950; Morris, 1967). The general equation of the rate constant for the uncatalyzed reaction is given by

$$k_2 = 7.6 \times 10^7 e^{-(7300/RT)} \qquad (6)$$

where R and T are as defined for k_1 above, and k_2 is the rate constant in liter/mol-sec.

Monochloramine also undergoes disproportionation (Morris and Weil, 1950; Morris, 1967) according to the reaction

$$2NH_2Cl \xrightarrow{k_3} NHCl_2 + NH_3 \qquad (7)$$

where the second order rate constant, k_3, in liters/mol-sec is expressed as

$$k_3 = 80e^{-(4300/RT)} \quad (8)$$

Granstrom (1954) has described a first order reaction which is the reverse reaction from monochloramine to hypochlorous acid, and it is given by

$$NH_2Cl + H_2O \xrightarrow{k_4} HOCl + NH_3 \quad (9)$$

where,

$$k_4 = 8.7 \times 10^7 e^{-(17,000/RT)} \quad (10)$$

and the unit of the rate constant is sec^{-1}.

A further reaction, the formation of trichloramine (Morris and Weil, 1950; Morris, 1967) can be:

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O \quad (11)$$

As the persistence of trichloramine occurs primarily below pH 4, it has limited sanitary significance. Chlorine also reacts with a large number of other compounds found in water. A number of these products which contain nitrogen, such as N-chloroglycines, are very poor disinfectants when compared to chloramine under identical test conditions.

CHLORINE DIOXIDE AS A DISINFECTANT IN WATER

Chlorine dioxide like chloramine does not react in aqueous solution to produce THM, it does not react with ammonia nor does it react to remove THM from solution. Relatively little work with chlorine dioxide has been done to accurately predict its reaction with the myriad of organic materials which may be found in a natural water. Chlorine dioxide destroys phenolic materials and has been used for taste and odor control in water supplies (Granstrom and Lee, 1958; Dowling, 1973). Limited data indicate that chlorine dioxide will produce quinones, chloroquinones, aldehydes, ketones, and epoxides depending upon the dose and organic material present (Stevens, Seeger and Slocum, 1976b; Dowling, 1973). The presence of humic and fluvic acids in natural waters may produce significant amounts of undesirable chlorine dioxide reaction products generating greater health hazards than THM production. The poly-phenolic compounds comprising humic materials would be expected to react with chlorine dioxide in a similar manner to aromatic compounds (Stevens, Seeger and Slocum, 1976b). It is not known if these potentially undesirable compounds will be produced in significant concentration by effective chlorine dioxide disinfection. In addition, the products of an interaction between chlorine dioxide and chlorophyll-a have not been assessed. Similar to the production of Term THM in the chlorination process, the effects of chlorine dioxide will depend upon the residual maintained and the concentration of organic material in the water. Eventual identification of products after disinfection is necessary for total evaluation of chlorine dioxide as a disinfectant.

Chlorine dioxide can be generated from sodium chlorite according to the following reactions:

$$5NaClO_2 + 4\ HCl \longrightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O \qquad (12)$$

or,

$$2\ NaClO_2 + Cl_2 \longrightarrow 2\ ClO_2 + NaCl \qquad (13)$$

In the last reaction a hypochlorite solution may be used in lieu of elemental chlorine. Production of chlorine dioxide in water treatment plants has generally been by the sodium chlorite method (Equation 13). To avoid unreacted sodium chlorite passing into the water supply the chlorine is always in excess (Dowling, 1973); thus, the disinfectant solution contains both chlorine and chlorine dioxide. Laboratory preparations can be scrubbed free of chlorine to produce pure chlorine dioxide solutions; however, there is a question in the literature (Dowling, 1973) regarding chlorine free production of chlorine dioxide by either reaction Equation 12 or 13.

Under water treatment conditions THM may be reduced without significantly affecting disinfection since chlorine dioxide reacts to remove the same precursors as chlorine (Miltner, 1977; Stevens, Seeger and Slocum, 1976) Differences in reaction rate are not known at this time. However, problems associated with chlorine dioxide, in addition to chloro-organic products, are the production of chlorite, chlorate and chloride. The toxicity of chlorite and chlorate is questionable. Musil and coworkers (1965) present evidence that chlorite produces methemoglobinaemia at relatively high concentration levels [>ten times maximum concentration levels set in several European countries (Dowling, 1973)]. Dowling (1973) relates chlorite to nitrate and states that under water treatment conditions no hazard exists. Both chlorite and chlorate are capable of the rupture of red blood cells (Miltner, 1977). Recent procedures for monitoring the levels of these species have been developed by the U.S. Environmental Protection Agency (Miltner, 1977).

Since chlorine dioxide is relatively stable under the reaction conditions, its disinfection efficiency should not be dependent upon rapid mixing. Geisser and Garver (1977) studied high-rate, high mixing energy input disinfection with five min detention times of stormwater and compared chlorine and chlorine dioxide as the disinfectants. They reported that chlorine dioxide appeared to be less sensitive than chlorine to mixing intensity and contact time.

To date, only a few studies have been conducted on the relative effectiveness of chlorine dioxide as either a bactericide or a viricide. In early studies the inactivation of poliovirus by chlorine dioxide was found to be more effective than either chlorine or ozone, and the inactivation when free chlorine or chlorine dioxide was present appeared to be dependent upon the system's redox potential (Dowling, 1973). In a review of work originally reported by Moffa and Smith (1974), Hoff (1978) presented data profiling poliovirus 1 inactivation by ClO_2 in a no-demand system. During a two min contact period, viral reductions of 0.5, 1.5, 2.0, and 3.5 $\log_{10}$ units for dosages of 0.2, 0.4, 0.6 and 0.8 mg/l ClO_2, respectively, were reported. In order to

achieve a 3 - 4 $\log_{10}$ reduction of cell associated poliovirus 1 within two min, ClO_2 dosages of 12 and 16 mg/l were employed by these same researchers. Chlorine dioxide has also been studied for its disinfection potential of combined wastewater overflows (Tifft et al., 1977). Four to five $\log_{10}$ reductions of exogenous poliovirus 1 were observed at ClO_2 dosages of 12 and 16 mg/l over a one min contact time. Additionally, 12 mg/l ClO_2 resulted in the same bacterial and viral kills as 25 mg/l chlorine in two min contact time in this test system. The effectiveness of chlorine dioxide as a viricide may be due to its higher affinity for adsorption on the virus protein coat leading to higher local concentrations on the surface (Dowling, 1973).

Less work has been done with regard to chlorine dioxide's effectiveness as a bactericide. Benarde et al. (1965, 1967) have shown that chlorine dioxide is an efficient bactericide in aqueous solution, possibly being slightly superior to free chlorine. One advantage of chlorine dioxide is that similar bacteriological results are obtained in systems with high or variable ammonia content. Comparison with breakpoint chlorination shows less control necessary to achieve similar results since chlorine dioxide does not react with ammonia (Dowling, 1973). Ridenour et al. (1947, 1949) have shown that chlorine dioxide is effective against vegetative bacteria and waterborne bacteria such as Eberthella typhosa, Shigella dysenteria, and Salmonella paratyphi B. More recently it has been suggested by Berndt (1965) that chlorine dioxide was not as efficient a bactericide as a 3:1 mixture of chlorine dioxide to chlorine. A synergistic reaction was postulated but this has not been examined under water treatment plant conditions. However, mixed disinfectants have produced successful bacteriological results in heavily contaminated water (Dowling, 1973).

DISINFECTANT MIXING

Most investigative work concerning rapid mixing and water streams has been directed towards either the role of rapid mixing together with the addition of a coagulent to optimize floc formation, or the role of rapid mixing together with the addition of chlorine to enhance the biocidal action of chlorine in a wastewater stream.

Levy and Ellms (1972) demonstrated the rapidity of mixing which can be obtained by introducing chemicals into a highly turbulent section of a pump. Vrale and Jorden (1971) investigated several rapid mixing schemes in their attempts to achieve complete homogenization of a coagulent with the stream to be treated. They concluded that a tubular, plug flow reaction was a much more efficient device for achieving rapid mixing than was a backmix reactor. They identified the important design considerations to be the points of chemical addition and the magnitudes of the turbulent scale and intensity in the mixing zone. The use of the average mixing velocity gradient (G) did not adequately describe rapid mix reactor performance. A similar conclusion was reached by Collins and coworkers (1971). Their rationale was that the disinfection process essentially consists of two steps, the first step being a very rapid mixing of the chlorine stream with the main stream, and the second step being dependent upon residence time distribution characteristics of the reactor (i.e., the perfect reactor performs as a plug flow reactor). Therefore they deduced that a large G in the second step may impede rather

than benefit the biocidal action of the chlorine, particularly in a reactor subjected to appreciable backmixing.

Gibson (1962) developed a technique to study mixing which employs the measurement of conductivity fluctuations in the turbulent field. He found that the experimental results for turbulent kinetic energy dissipation were in good agreement with a decay law developed by Batchelor and Townsend (1948). Certain concepts developed by Gibson were extended by Stenquist and Kaufman (1972) to wastewater disinfection using a grid bar mixer for chlorination. They found that non-backmixed (tubular) reactors, given similar chlorine and wastewater stream characteristics, initially achieved a greater degree of coliform inactivation. However, at the end of contact times normally found in field practice, the amount of inactivation achieved using non-backmixed and backmixed reactors was essentially the same. Stenquist and Kaufman (1972) cited two reasons why a tubular reactor is superior to a backmixed reactor:

1. Backmixing apparently results in a chlorine residual with poorer bactericidal effectiveness because of reaction of the chlorine entering the reactor with residuals previously formed, and

2. Short-circuiting, or the presence in the effluent from the reactor of fluid particles with a very short chlorine contact time relative to the mean contact time, can greatly affect overall performance.

The latter condition is prevented by a tubular reactor. Longley (1974), chlorinating a wastewater stream, achieved very good bactericidal efficiencies using a plug flow reactor. However, the bactericidal efficiencies achieved in the conventional backmixed chlorine contact chamber after the requisite contact time (approximately 12 - 15 min) approached those achieved with rapid mix of the chlorine solution. In all instances rapid mixing promoted superior bacteriophage inactivation. The viruses apparently were inactivated by hydrochlorous acid and were relatively stable in combined chlorine concentrations up to 10 mg/l.

SECTION 5

METHODS AND MATERIALS

WATER TREATMENT PLANT

The site for this study was the new water treatment plant (WTP) of the City of Boerne, Texas. The WTP is located at a newly constructed reservoir and went on-stream in January, 1979, when the water level in the reservoir was sufficient to permit withdrawal through the collection works. The Boerne City Reservoir is an impoundment contained by the John D. Reed dam northwest of the City of Boerne in Kendall County, Texas, approximately twenty miles northwest of San Antonio. Table 2 gives the characteristics of the reservoir. The dam was constructed by the U. S. Soil Conservation Service (USSCS, 1968a,b) for the primary purpose of flood control, however, the City of Boerne located its water treatment plant on the reservoir to provide additional water to the city. The reservoir is fed by run-off from the Cibolo Creek watershed encompassing an area of 5.06×10^7 m^2 (12,500 acres) which is characterized by a low population density with vegetation typically being grasses, oak and cedar. The length of the drainage basin behind the John D. Reed dam is approximately eight miles and the average breadth is two and one-half miles. The drainage area is 5.123×10^7 m^2 (12,656) acres. The highest elevation (672 m) occurs in the western end of the drainage basin and the watershed drains from west to east through some 52 mi total of established channels. The main channel follows a meandering course in an easterly direction for about eleven miles.

In the upland areas of the basin several springs exist which contribute continuous flow to the creek. These springs include Champee Spring and Brown Spring as well as others unnamed. The watershed is within the Edwards Plateau Land Resource Area (USSCS, 1978a); most of the watershed is within the outcrop of the upper member of the Glen Rose formation, Trinity group (Adams, 1978). Most of the soils of the watershed are fine textured, slowly to moderately permeable, shallow and rocky. The dominant soil series are Crawford, Denton, Tarrant, Brackett, Frio, Krum and Lewisville. The principal use of the watershed is livestock grazing, although limited development within the watershed, particularly near the reservoir, is underway. Generally the development is confined to single unit dwellings which use septic tanks for domestic wastewater disposal. The reservoir is available for limited recreational use including swimming, boating (electric motors only), and fishing.

The treatment train (Figure 1) of the 6056 m^3/d (1.6 mgd) WTP consists of prechlorination, alum coagulation and sedimentation through an upflow clarifier, pressure sand filtration, and post chlorination. Gas fed chlorinators are used for chlorination and facilities are available for

TABLE 2. Characteristics of the Boerne Reservoir Dam

Characteristics	Measurement
Drainage area	51.18 km^2 (19.76 sq mi)
Elevation, top of dam	473.84 m (1554.6 ft)
Maximum height of dam	27 m (89 ft)
Length of dam	1593 m (5,225 ft)
Volume of fill	1.1981×10^6 m^3 (1,198,100 cu yd)
Total capacity	1.078×10^7 m^3 (8736 ac ft)
Sediment	1.382×10^6 m^3 (1120 ac ft)
Municipal use	3.70×10^6 m^3 (3000 ac ft)
Retarding pool	5.694×10^6 m^3 (4616 ac ft)
Surface area	1.39×10^6 m^2 (344 acres)
Average depth	11 m (37 ft)
Principal spillway elevation	14.1 m (46.1 ft)
Residence time	206 days
Operating pool	4.934×10^6 (4000 ac ft)

Source: United States Soil Conservation Service, 1968b.

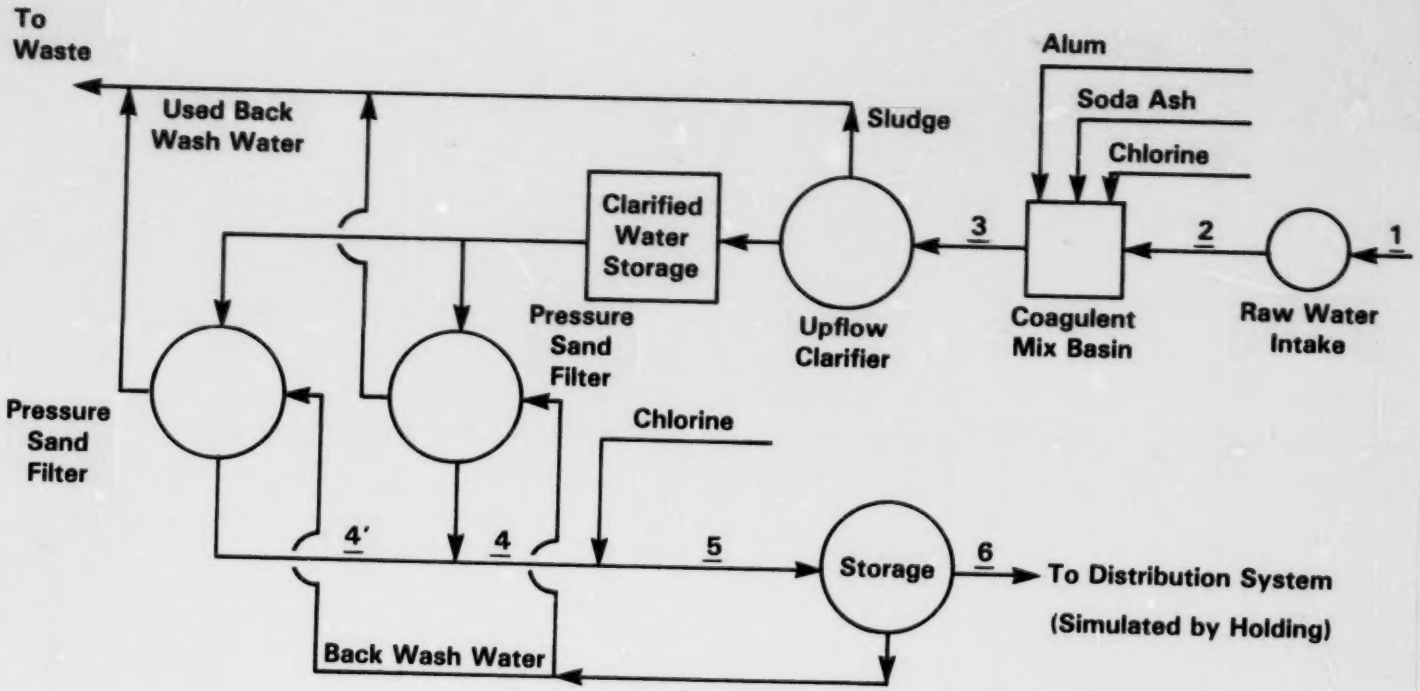

FIGURE 1. Treatment Train of 1.6 MGD Boerne Water Treatment Plant

fluoridation. Disposal of sludge, filter backwash water, and other plant liquid waste streams is into two nearby evaporation ponds.

As shown by the sampling matrix in Table 3, the WTP was evaluated monthly during the study period in order to develop baseline disinfection and THM formation data relating to "standard operational" practices.

PROTOTYPE SYSTEM

Filtered, nondisinfected water was used for this study. Normal prechlorination of the WTP's main water stream has not been consistently practiced. However, when it was employed, prechlorination was discontinued in sufficient time prior to the initiation of a data-gathering run to preclude a source of in-plant THM formation.

Figure 2 is a schematic of the prototype disinfection system. The filtered, nondisinfected water was fed to a 1890 l (500 gal) storage tank and pumped through the prototype system at a flowrate of 4.7 l/s (75 gal/min). Provisions were available for "seeding" the water stream prior to disinfection. Determination of seeding requirements for the prototype system was based upon the levels of indigenous organisms found in the test water. Seeding experiments were performed to evaluate the prototype system since indigenous organism levels were insufficient to insure statistical significance in the evaluation of disinfection effectiveness.

Aqueous chlorine, chlorine dioxide and ammonia were peripherally injected into one of two plug-flow mixers which had internal throat diameters of 20 mm (0.8 in) and throat lengths of 0.91 m (3 ft). Downstream from each mixer the water stream passed through an energy recovery section of 0.91 m (3 ft) into a 100 mm (4.0 in) internal diameter (ID) pipe (PVC, schedule 80). The total length of the prototype system was 37.36 m (122.6 ft). For a flow rate of 4.7 l/s (75 gal/min) the Reynolds numbers of the 20 mm (0.8 in) and 100 mm (4.0 in) sections are 370,000 and 74,200 respectively. Studies involving the addition of chlorine followed by ammonia or ammonia followed by chlorine were performed by addition of the second chemical into the second mixer located 8.78 m (28.8 ft) feet downstream from the first mixer. This permitted 15 sec mean contact with free chlorine or ammonia prior to initiation of chloramine formation. Total mean contact time between the addition of the disinfectant and the discharge of the water stream was approximately 60 seconds.

Addition of a seed organism was accomplished at the suction side of the system pump (organisms were not introduced into the holding tank).

Sampling

Samples having a contact time of approximately one sec were collected at the end of the mixer throat, and samples with a mean contact time of 60 sec were collected at the discharge of the pipe contactor. Samples with desired contact times greater than 60 sec were collected in glass or plastic containers, as appropriate, at the discharge point. After the predetermined contact time had elapsed, a suitable reducing agent was added to quench the disinfecting agent. Additionally, a sampling port immediately prior to the

TABLE 3. Sampling Matrix for Boerne Water Treatment Facility

Sampling Point	Disinfectant Dose	Sampling Frequency	Routine Parameters Monitored
1. Reservoir	As	Once	Chlorine Residual
2. Pretreatment	System	Each	Standard Plate Count
3. Pre-Disinfection	Is	Month	Total Coliform
4. Post-Disinfection	Operated		Total Trihalomethane (InstTHM)
5. Clear Well			Total Trihalomethane (TermTHM)
6. Distribution System			Total Trihalomethane formation potential (TTHMFP)
			Chlorophyll-a
			NH_3 - Nitrogen and TKN
			Temperature
			Alkalinity
			pH
			Turbidity and Color
			Total Organic Carbon

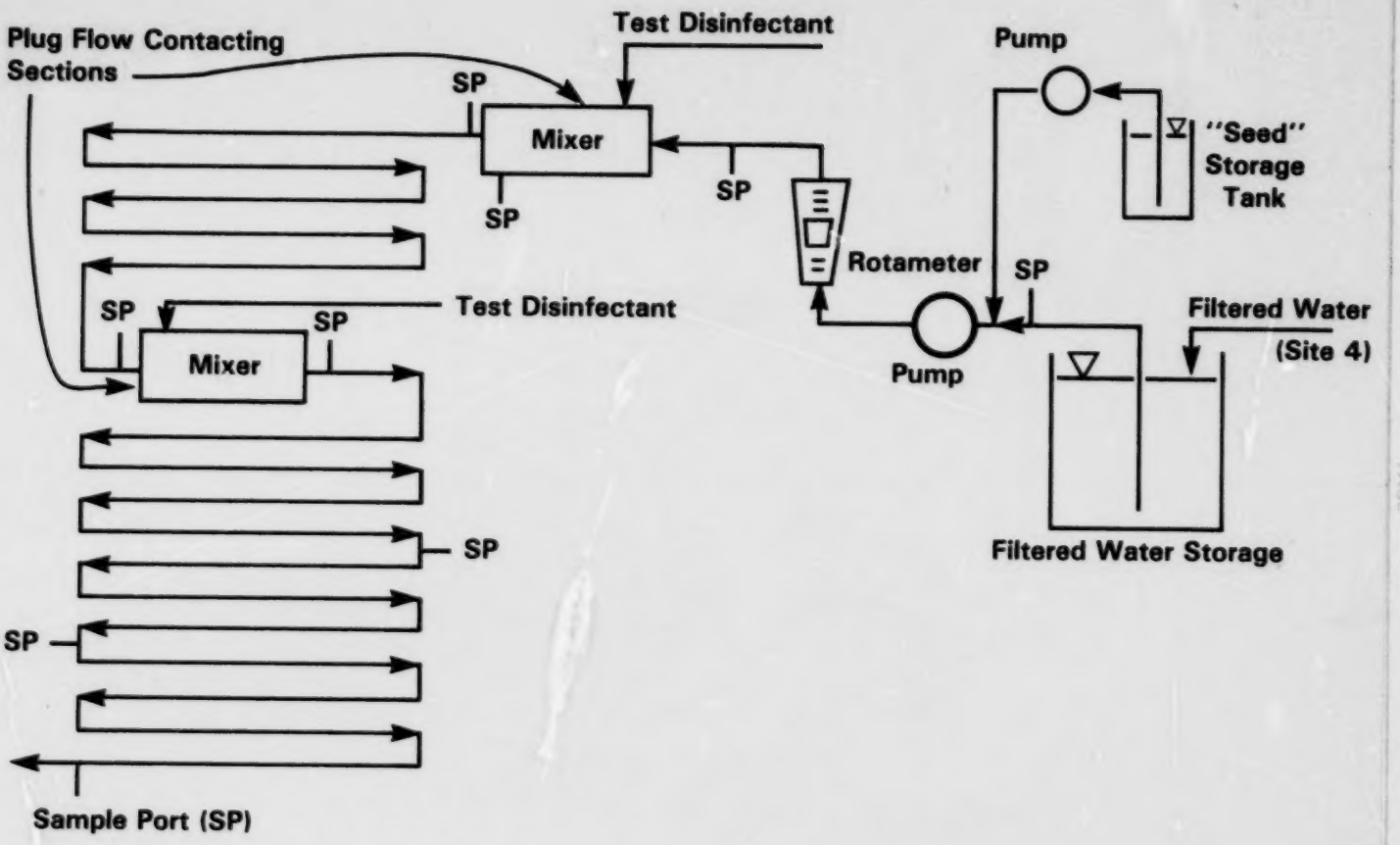

FIGURE 2. Schematic of Prototype Disinfection System

second mixer (the point of ammonia or chlorine addition) allowed sample collection for evaluation of disinfectant residual and THM formation immediately prior to either chlorine or ammonia addition for the chloramination studies. Overall control samples were obtained from a sample port immediately upstream from the first mixer.

The sampling matrix and the chemical and physical parameters monitored for the prototype disinfection system are shown in Table 4.

BACTERIOLOGICAL ANALYSES

Collection of the bacteriological samples was accomplished in 500 ml polypropylene bottles that were cleaned, rinsed with distilled water and autoclaved to insure sterility. Water samples containing residual chlorine were collected in sterile 500 ml bottles containing sodium thiosulfate (0.01%). Care was taken to avoid contamination upon sample collection by proper handling of the bottle and cap. After labeling, the samples were placed in wet ice at 4°C until analysis.

Standard Plate Count

The appropriate serial dilutions of the sample were prepared in phosphate buffered saline and plated in triplicate using Plate Count Agar (Difco) (Standard Methods, 1975). Plates were placed in a 35°C ± 0.5°C incubator for 48 hr. Only plates showing 30 - 300 colonies were considered in determining the standard plate count. If colonies per plate in the highest dilution exceeded 300, results were recorded as greater than 300 times the appropriate dilution factor. Likewise, if no chosen dilution had colonies, the results were recorded as less than one colony per lowest dilution. Counts were reported as colony forming units per milliliter (cfu/ml).

Total Coliform

Total coliform densities were determined by the membrane filtration technique (Standard Methods, 1975). Triplicate volumes of undiluted or diluted samples were filtered, the filters were placed on m-Endo agar LES, and the plates were incubated at 35°C ± 0.5°C for 20 - 24 hr. Plates showing 20 - 80 typical coliform colonies were used in the calculation of total coliforms/100 ml.

Fecal Coliforms

Fecal coliform levels were monitored in the reservoir using a membrane filtration technique. Water samples were filtered in triplicate through 0.45 micron Gelman GN-6 membrane filters which, in turn, were placed on m-FC agar in 60 mm plates. Plates were incubated for 4 hr at 35°C ± 0.5°C and then transferred to a 44.5°C incubator for the remaining 24 hr period. Typical blue colonies were counted and reported as fecal coliform/100 ml.

Fecal Streptococci

The levels of fecal streptococci in the reservoir were determined by

TABLE 4. Sampling Matrix for Prototype Disinfection System Runs

Disinfectant Dose	Disinfectant System	Sampling Time	Routine Parameters Monitored
0.5 mg/l	Chlorine	0	Disinfectant Residual
1.5 mg/l	Chlorine plus Ammonia	1 sec	Standard Plate Count
5.0 mg/l	Ammonia plus Chlorine	15 sec	Total Coliform
	Chlorine Dioxide	31 sec	Total Trihalomethane (InstTHM)
		1 min	Total Trihalomethane Formation Potential (TTHMFP)
		15 min	Chlorophyll-a
		60 min	NH_3 - Nitrogen and TKN
			Temperature
			Alkalinity
			pH
			Turbidity and Color
			Total Organic Carbon
			Chlorate and Chlorite+

+ Runs with chlorine dioxide as a disinfectant only

filtering water samples in triplicate through 0.45 micron Gelman GN-6 filters. Membrane filters were placed on m-Enterococcus agar and incubated at 35°C ± 0.5°C for 48 hr. Red to pink colonies were counted, and densities were reported as fecal streptococci/100 ml.

Coliphage

Indigenous coliphage were detected using Escherichia coli K13 as the host organism. Appropriate volumes of sample and 0.2 ml of an 18-hr aerated broth culture of E. coli K13 were added to 3.5 ml of liquified, 1% tryptose phosphate agar (TPA). This volume was poured over a solidified TPA base layer (1.5% agar) and incubated at 35°C ± 0.5°C for 18 - 20 hr. Plaques were scored and reported as plaque-forming units (pfu)/liter.

SEED ORGANISMS

Coliform Bacteria

The coliform bacteria chosen as a seed organism for the prototype disinfection system is unique in that it carries a lambda (λ) phage integrated into its chromosome. In the case of E. coli lys 147, this prophage state is maintained by a heat-sensitive repressor. At 30°C this bacteria grows normally. However, if the organism is exposed to a higher temperature for a relatively short period of time (e.g. 42°C for 3 - 4 hr), the repressor protein is inactivated and the phage is excised from the bacterial chromosome. From this point a lytic phage infection is established, and, ultimately, the E. coli cell is lysed with concomitant release of infectious viral particles.

These attributes allow the use of a coliform bacteria in the disinfection tests which were measured as a viral plaque forming unit (pfu). At the same time, indigenous standard plate count bacteria were enumerated on the sample by "self-destructing" the seed organism.

In practice, an appropriate volume of sample was plated in yeast extract (.5%) - NaCl (.5%) - tryptose (1%) - $MgSO_4$ (.001 M) agar (YET) using a classical soft agar overlay technique (Adams, 1959) with E. coli 2e0lc (λ sensitive) as the indicator organism. Concurrently, each sample was assayed using the protocol for standard plate count (Standard Methods, 1975). All plates were incubated at 42°C for 3 - 4 hr followed by a shift down to 35°C. After approximately 18 hr, pfu reflecting the initial presence of E. coli lys 147 were counted. The level of indigenous bacteria observed as viable colony forming units (cfu) was recorded at 48 hr as the standard plate count.

Cultures of E. coli lys 147 were grown in YET broth. Flasks were placed on a rotary shaker (200 rpm) at 30°C overnight. Cells were collected by light centrifugation (2,000 g for 5 min) and resuspended in sterile 0.85% NaCl for seeding.

Bacteriophage f_2

Seed stocks of bacteriophage f_2 were pooled from lysates prepared by either a broth method or a plate method. In all cases, E. coli Hfr Hayes

was used as the host organism. For preparation of f_2 using a broth culture, 100 ml of log-phase E. coli cells grown in tryptose phosphate broth (TPB) were pelleted by light centrifugation (1500 x g for 3 min) and resuspended in the centrifuge tube with 5 ml of TPB containing f_2 resulting in a final multiplicity of infection (MOI) of one pfu/cell. After a 15 min attachment period with intermittent vortexing, additional TPB was added to a final volume of 20 ml. The infected cells were transferred to a sterile 250 ml Erlenmeyer flask, placed on an incubator shaker (35°C) and mixed at 200 rpm for 3 - 4 hr. At this time one ml of chloroform was added to the culture which was returned to the shaker for 15 min. Subsequently, cell debris was removed by centrifugation in glass tubes at 3000 x g for 10 min. Supernatant containing f_2 was collected and stored at 4°C until use.

The plate method of phage stock preparation involved inoculating tubes containing soft agar overlay (0.8% agar in TPB) with 0.2 ml of an overnight E. coli Hfr Hayes culture and 0.2 ml of the near-confluent lysis dilution of f_2. This overlay was distributed over previously prepared base-layer plates (1% agar in TPB). Plates were incubated at 35°C overnight. After addition of 3 ml TPB/ plate, the f_2-containing soft agar was scraped off into a Ten Broeck tissue homogenizer. This mixture was homogenized using three to four pestle strokes. Chloroform was added to the pooled homogenates (1 ml/20 ml of homogenate) which then was mixed vigorously. The phage lysate was recovered by centrifuging the homogenate as described above. The supernatant fraction was held at 4°C until use.

Bacteriophage f_2 stocks were pooled and titrated 48 hr prior to use in seeding experiments. Plaque assays were done as described for indigenous bacteriophage except that E. coli Hfr Hayes was employed as the host organism. Phage lysates generally contained $10^{10} - 10^{11}$ pfu/ml.

DISINFECTANT SYSTEMS

Sodium thiosulfate was employed to quench the disinfectants at the desired times for all bacteriological and THM analyses. The quantity of reducing agent depended upon the disinfectant dose, but was always in excess.

Disinfectants were introduced into the mixers through a vacuum ejector and chlorine and ammonia were fed as gases. Chlorine dioxide was fed as an aqueous solution prepared by reacting sodium chlorite with hydrochloric acid in a contact chamber filled with glass beads (5 min detention time).

Field analyses for residual chlorine, total chlorine, chloramines, and chlorine dioxide were performed by either amperometric titration (Fischer and Porter Model 17T1010) or colorimetric determination with N,N-diethyl-p-phenylene-diamine sulfate (DPD). Ammonia determinations in the field were done colorimetrically with Nessler's reagent.

CHEMICAL ANALYSES

Temperature and pH were measured in the field at the WTP sampling points. For prototype runs these parameters were measured at the field location as

well as after transport to the analytical laboratory. All samples for routine chemical analyses were collected in one-liter plastic bottles and stored at 4°C for transport to the laboratory.

Alkalinity, turbidity (DRT-100, H. F. Instruments), and total organic carbon (Beckmann Model 915A carbon analyzer, Model 865 infrared analyzer) were measured as described in Standard Methods (1975). Preservation of the TOC samples was required if analyses could not be performed immediately. This was accomplished by addition of 0.1 ml concentrated hydrochloric acid per 5 ml of sample. The acidified samples were stored at 4°C until analyzed.

Ammonia-nitrogen (NH_3-N) was determined by utilizing the automated alkaline phenolate procedure as described by the Environmental Protection Agency (1976) and modified for low level concentration Auto Analyzer® II system. Total Kjeldahl nitrogen (TKN) was determined by digestion (Technicon Block Digestor, DB-20), dilution to volume, and analysis on the Technicon system (EPA, 1976). Preservation, if necessary, was accomplished for both NH_3-N and TKN samples by addition of 0.03 ml of a 0.15 M solution of mercuric chloride per 30 ml of sample. Samples were stored at 4°C until analyzed.

Chlorophyll-a concentrations were determined by the fluorometric assay (Farrand A-4 filter fluorometer, 5-60 excitation and 2-28 emission filters) method as described in Standard Methods (1975).

Trihalomethane Analyses

Samples were collected in 40-ml vials with (Instant THM) or without (Terminal THM) sodium thiosulfate and sealed with teflon®-faced septums. Instant THM Samples were stored at 4°C and Terminal THM Samples were stored at room temperature in the dark until analysis or until the designated times for quenching by thiosulfate.

THM samples were analyzed by gas chromotography using the gas sparging technique developed by Bellar and Lichtenberg (1974). Samples (5 ml) were sparged for 20 min at 25°C with a 30 ml/min flow of grade six helium carrier gas and collected on a Tenax trap (30.5 cm long; 0.318 cm OD; 0.293 cm ID). Thermal desorption at 210°C with a 20 ml/min helium flow onto a 50°C analytical Tenax column (60/80 mesh; 2.4 cm long, 0.31 cm OD, 0.216 cm ID) was then accomplished. The analytical column was held isothermally for 6 min and temperature-programmed to 250°C at a rate of 10°C per min. Typical retention times of 14.40, 16.38, 18.24 and 20.02 min for chloroform, dichlorobromomethane, chlorodibromomethane and bromoform, respectively, were exhibited for this analytical column. All analyses were performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector and a CDS 111C reporting integrator.

SECTION 6

RESULTS

FIELD STUDIES

Reservoir

Baseline data on the raw water supply for the Boerne WTP were collected during the testing period. Figure 3 shows the variation of depth at the principal spillway from January, 1979 through August, 1980, and Figure 4 shows the monthly and accumulated rainfall over the same period. Organic loading due to runoff from the watershed was minimal.

Both chemical and microbiological measurements were performed to ascertain the quality of water entering the WTP. Two sites were chosen for analysis (sites 1 and 2 on Figure 1). Site 1 samples were surface grab samples taken monthly from a point on the shoreline above the intake structure for the WTP. Site 2 samples were taken from the WTP inlet before the raw water was subjected to chemical addition and entered the clarifier (see Figure 1). Site 2 samples approximate those which would come from below the surface of the reservoir since the inlet pipes are at several depths and converge prior to the sampling point. The inlet pipes are below a gravel layer causing a certain degree of filtration. Tables 5 and 6 show the results of the chemical analyses.

The ammonia-nitrogen (NH_3-N) and TKN measurements are plotted in Figure 5. The observed levels are close to the detection limits of the methods employed. Consequently, the variations observed are not considered significant. Nitrogen loading of the reservoir appeared primarily as organic nitrogen.

Figure 6 shows the variation in total alkalinity and total dissolved solids (TDS) during the study period. Estimates of the TDS values were obtained by calculation (specific conductivity equals the total dissolved solids times two, [Adams, 1978]). The values obtained varied as the reservoir filled and are within the expected ranges for this type of containment and watershed. Turbidity measurements were very low and showed no significant trends. This supports the observation that variations were due to the filling of the reservoir.

Total and fecal coliform and fecal streptococci values were determined at sampling sites 1 and 2. Table 7 shows that there was no significant human pollution during the study period. The fecal coliform to fecal streptococci ratios suggest nonhuman sources of bacterial contamination. The present land

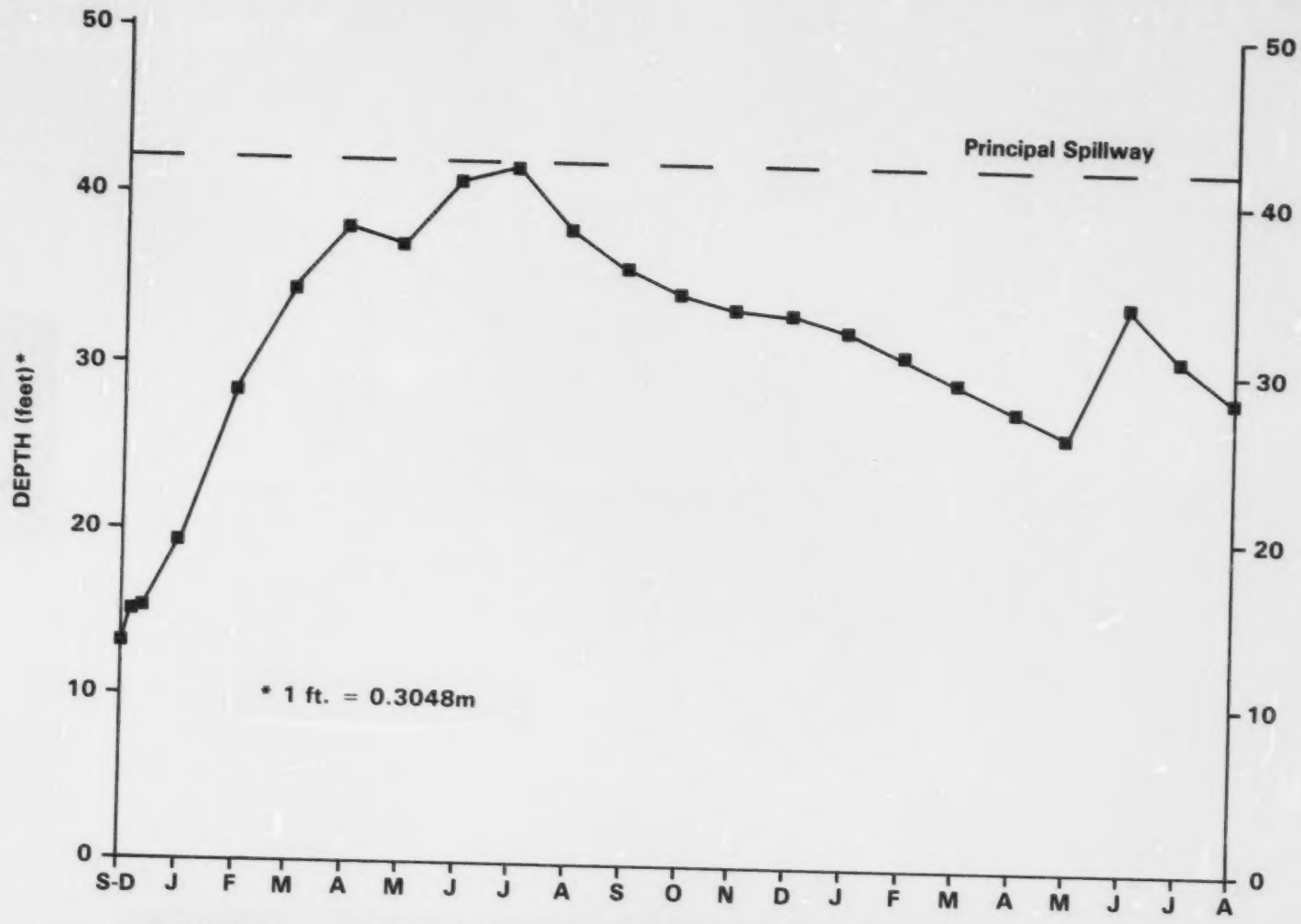

FIGURE 3. Depth of Boerne Reservoir from September 1979 to August 1980

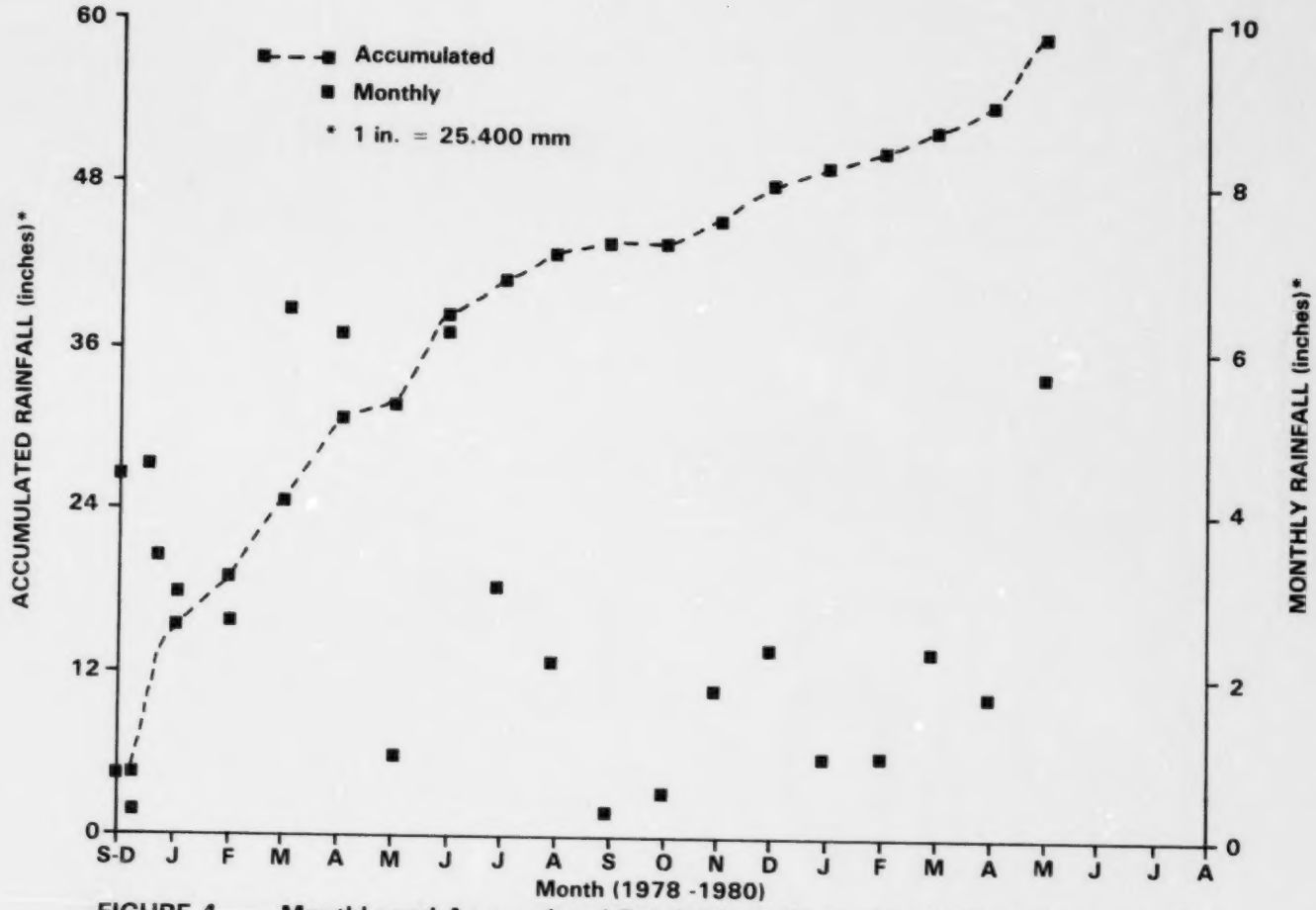

FIGURE 4. Monthly and Accumulated Rainfall from September 1979 to August 1980

TABLE 5. Boerne Reservoir Chemical Data (Sampling Site 1)

Date	Field pH	Temperature (°C)	Turbidity (NTU)	TOC (mg/1)	TKN (mg/1)	NH_3-N (mg/1)	Chloro-phyll-a (mg/1)	Total Alkalinity (mg/1 as $CaCO_3$)	Specific Conductivity (μmho/cm^2)	TSS (mg/1)
2-13-79	8.05	12.00	1.60	10.0	0.40	0.01	1.5	211	430	
3- 6-79	7.87	14.00					9.6			
3-20-79				4.0	0.30	0.01	16.4	210	439	
4- 2-79		16.00	1.70	4.0	0.40	0.02	9.4	193	421	
4-17-79	7.21	20.50	0.67	3.0	<0.20	0.02	13.5	193	415	
4-24-79	7.58	23.00					13.8			
4-26-79	7.71	24.00	5.20	2.0	0.10	<0.01	13.6	183	377	
5-15-79	7.64	23.00	1.30	5.0	0.20	<0.01	30.2	180	380	
5-22-79			1.30	2.9			10.2	172	368	
5-29-79			1.00	3.5	0.30	0.02		170	375	
6- 5-79			1.80	2.6	<0.20	0.02	12.7	162	346	
6-12-79	8.37	27.00	1.10	3.7	0.20	<0.01	7.6	169	360	
6-19-79	7.30	25.00	0.82	4.1	0.20	<0.01	12.6	165	356	3.1
6-26-79	7.34	28.00	0.82	5.4	0.20	<0.01	13.1	164	354	2.9
7-10-79			0.68	3.6			5.4	151	346	2.3
7-17-79			0.64	3.4	0.40	0.02	3.7	161	348	2.3
7-24-79	6.80		0.51	4.0	0.30	0.02	4.5	160	344	1.4
7-31-79			0.57	3.0	0.30	0.01	6.2	157	347	2.5
8- 7-79			0.90	3.0	0.50	0.01		151	347	3.4
8-14-79		27.60	1.00	2.0	0.20	<0.01		150	335	
8-22-79			0.26	3.0	0.30	<0.01		150	345	
9-18-79	7.80	24.60	2.20	4.0	0.80	0.02	4.7	153	331	15.8
9-23-79	8.15	26.80								
10- 9-79	8.10	23.60	0.96		0.80	0.03	10.3	147	340	2.5
11-13-79	7.75	17.00	4.53	3.4	0.38	<0.01	5.7	149	370	7.8
12- 4-79	7.85	12.80	1.63		0.30	0.02	5.8	144	375	2.1
1-14-80	7.85	11.20	1.68		0.30	<0.02	22.0	142	366	3.7
2-22-80	8.63			4.7	0.20	<0.02		149	375	77.2
3-11-80	8.43	7.95		3.2	0.20	0.03		143	374	4.6

TABLE 6. Boerne Reservoir Chemical Data (Sampling Site 2)

Date	Field pH	Temperature (°C)	Turbidity (NTU)	TOC (mg/l)	TKN (mg/l)	NH_3-N (mg/l)	Chloro-phyll-a (mg/l)	Total Alkalinity (mg/l as $CaCO_3$)	Specific Conductivity ($\mu mho/cm^2$)
5-15-79	7.53	2.0	0.47	2.0	0.40	0.03	5.7	187	400
5-29-79	7.80	22.0	0.65	3.6	0.20	0.03		178	395
6-12-79	7.59	25.0	0.48	2.5	0.20	0.03		181	385
6-19-79	7.76	23.2	0.38	2.4	0.50	0.02		164	364
6-26-79	7.81	26.8	0.36	2.4	0.20	0.02		173	379
7-24-79	7.91	26.4	0.35	3.0	0.20	<0.01		164	357
7-31-79	7.81	27.0	0.41	2.0	0.60	0.01		159	354
8-14-79	8.10	25.5	0.30	2.0	0.20	<0.01		150	335
9-18-79	7.97	22.3	0.41	2.0	<0.20	<0.01	2.0	150	330
10-9-79	7.96	20.5	0.33				2.0	146	343
11-13-79	8.03	13.2	1.23	3.4		<0.01	2.7	145	372
3-11-80	7.95	6.5	1.40			0.02		149	377

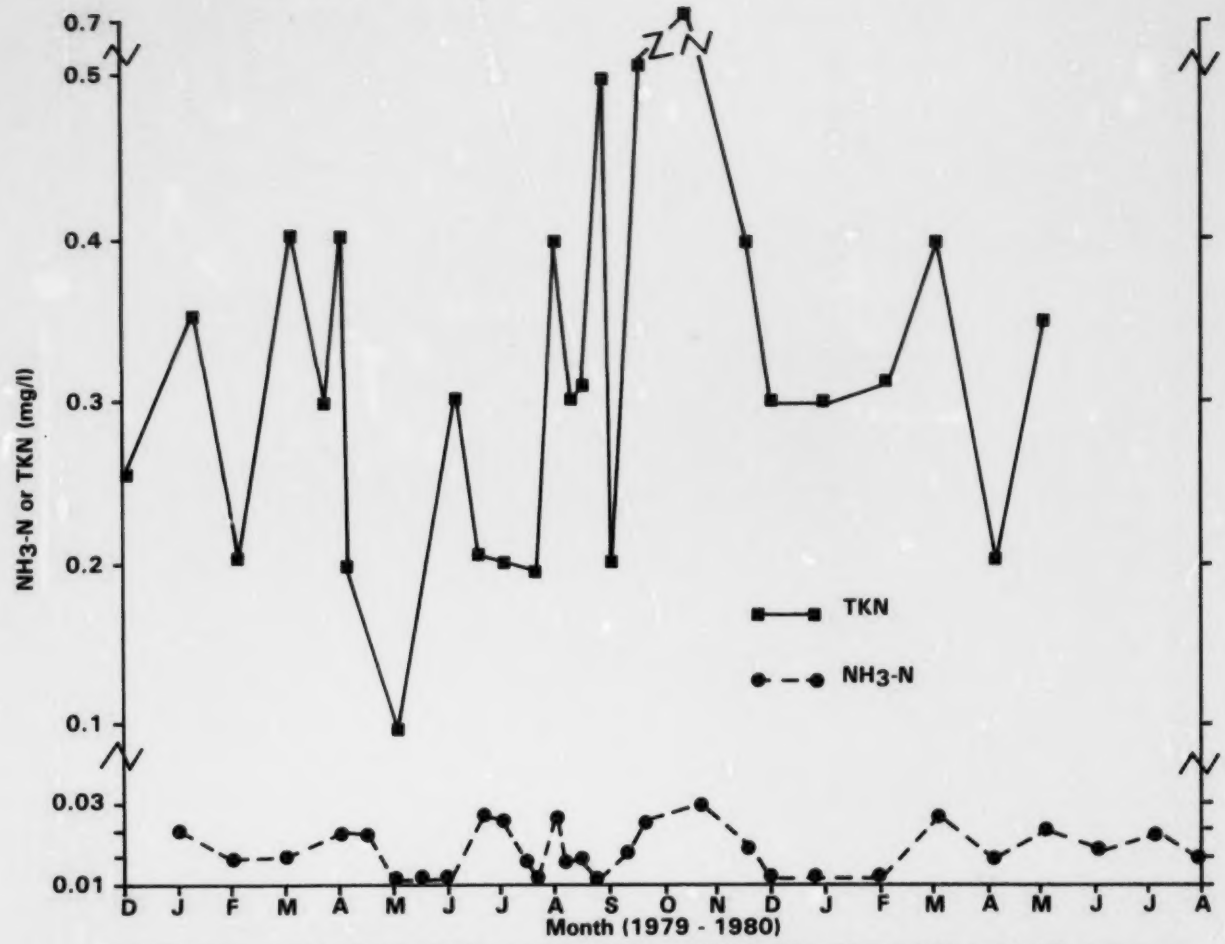

FIGURE 5. Variation of Ammonia Nitrogen (NH_3-N) and Total Organic Nitrogen (TKN) Levels in Boerne Reservoir from December 1979 to August 1980

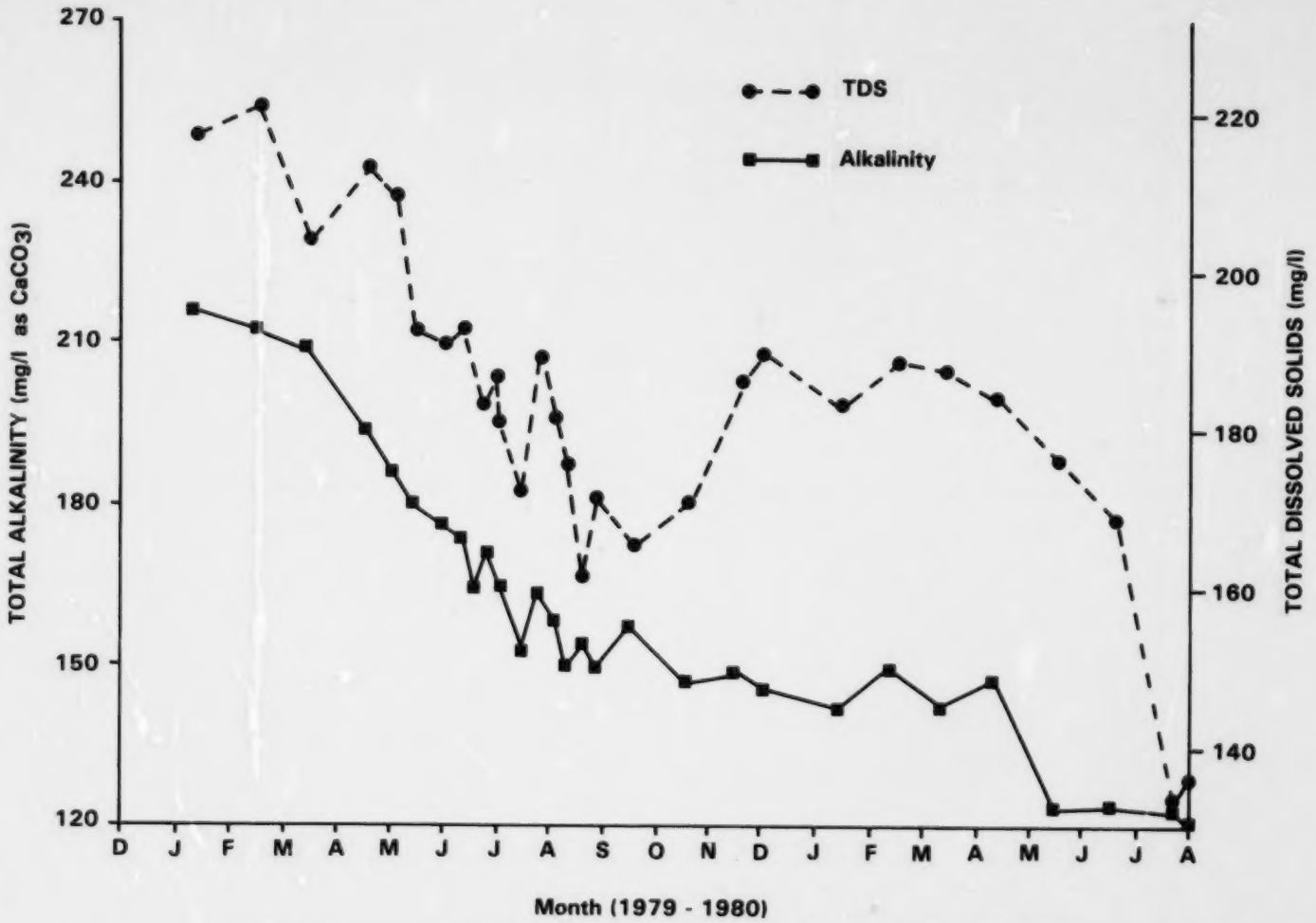

FIGURE 6. **Total Alkalinity and Total Dissolved Solids Levels in Boerne Reservoir from January 1979 to August 1980**

TABLE 7. Boerne Reservoir Microbiological Quality (Sampling Site 1)

Sampling Date*	Total Coliform (cfu/100 ml)	Fecal Coliform (cfu/100 ml)	Fecal Streptococci (cfu/100 ml)	Coliphage† (pfu/1)
1979				
5-15	4	1	8	<25
5-22	9	1	18	<25
5-29	34	<0.3	2	<33
6-5	9‡	61‡	63	230
6-12	97	2	1.7	76
6-20	4	2	1	50
6-26	1	0.3	3	<25
7-10	10	<0.3	1	<25
7-17	4	0.3	0.3	<100
7-24	9	1	3	<25
7-31	1	1	1	<25
8-14	150	26	46	<100
9-18	62	17	56	<50
10-9	7	2	2	-
11-13	41	10	5	-
12-4	6	7	1	<50
1980				
1-14	<0.3	2	-	-
2-21	6	1	4	-
3-11	9	0.7	5	-
4-8	16	11	84	<25
5-13	39	25	**	100
6-17	2	0.3	1	-
7-29	4	4	7	-
8-13	22‡	35‡	21	-

* Surface grab samples

† *E. coli* K13 as host organism

‡ Questionable values as FC > TC

** Inadequate sample volume

use in the watershed is approximately 80% rangeland, and this supports the observation that the biological characteristics resulted from rangeland runoff.

Water Treatment Plant

Baseline data collected during the normal operation of the WTP showed little variability in chemical or bacteriological parameters during the testing period. Table 8 shows the average chemical addition during the period of study. The variations in operating conditions were due primarily to problems associated with bringing the plant on-line and developing experience to provide the most effective operation. After this initial period of fluctuation (ca. six months), the chemical parameters showed almost no changes.

Table 9 illustrates the ranges of bacteriological and THM data observed since the sampling program began in early 1979. All of the high coliform and standard plate count (SPC) values were observed during the first six months of operation. Since September 1979 there has been <.33 cfu/100 ml total coliform (TC) and <.2 cfu/ml SPC at the post-chlorination sampling site and in the simulated (24 hr hold) distribution samples. The reservoir exhibited a characteristic change in TC from a high level of 150 cfu/100 ml in August 1979 (~9000 cfu/ml, SPC) to 9 cfu/100 ml in March 1980 (120 cfu/ml, SPC) due primarily to the colder weather.

The observed range of THM data (Table 9) follows the same general trends with higher levels observed during the first six months of operation. During the last four months of the study the chlorine dose and residuals (Table 8) were relatively constant averaging 2.37 mg/l and 1.14 mg/l, respectively. Furthermore, TOC levels at the chlorination site did not change greatly (2 - 5 mg/l). Consequently, the Term THM levels during this period were relatively constant (85.1 $\pm$ 5.3 µg/l). Figure 7 shows the monthly variation in both TOC, chlorophyll-a and THM levels from March 1979 to August 1980.

To quantitate the optional hold times for the terminal THM levels as well as to show the characteristic behavior of the reservoir with regard to THM production, THM growth curves were constructed periodically during the study period. Figure 8 shows an average THM production curve. Hold times of 36 to 48 hr are on the stable portion of the curve. Consequently, simulated distribution samples and Term THM samples were held for a minimum of 36 hr.

Other chemical paramaters (Table 10) have shown relatively little change during plant operation. Again, the greatest variaton in the data was observed during the first six months of operation. The consistency of the reservoir water and the plant operation has resulted in a stable system. The total rainfall into the watershed was 312 mm (12.3 in) from July 1979 to August 1980 (average 38.9 mm or 1.53 in per month). The reservoir depth reached a maximum of 12.2 m (40 ft) during July and thereafter steadily declined. The relatively small amount of runoff to the reservoir may partially explain the stability observed, since organic addition to the system was low.

TABLE 8. Chemical Addition for Normal Operation of Boerne WTP from December 1979 to August 1980

Dose Range	Chemical Added			
	Alum mg/l	Lime mg/l	Chlorine Dose mg/l	Free Chlorine Residual mg/l
Maximum	20.0	5.0	2.47	2.30
Minimum	10.0	0.0	2.23	1.10
Average	12.2	2.8	2.37	1.14

TABLE 9. Range of Bacteriological and Trihalomethane Data at Sampling Sites in Boerne WTP from February 1979 to August 1980

Sampling Site	Total Coliform (cfu/100 ml)	Standard Plate Count (cfu/ml)	TTHM (µg/l)
Reservoir (Site 1)	<.33 - 150	51 - 9000	<.1
Pretreatment (Site 2)	0.33 - 38	80 - 380	<.1
Post-coagulation (Site 3)	0.33 - 52	0.6 - 430	<.1
Post-filtration (Site 4)	5 - 60	10 - 1700	<.1 - 3
Post-chlorination (Site 5)	<.33 - 4	<.2 - 43	58 - 137

TABLE 10. Ranges of Chemical and Physical Parameters for Normal Operation of Boerne WTP from March 1979 to August 1980

Sampling Point	Turbidity (NTU)	pH (units)	TOC (mg/1)	Temp °C	TKN (mgN/1)	NH_3 (mgN/1)	Total Alkalinity (mg/1 as $CaCo_3$)	Specific Conductance (μmhos/cm)	Chlorophyl- a (μg/1)
Reservoir (Site 1)	.50-5.2	8.1-8.6	2-12	11-24	<.1-.5	<.01-.02	142-180	340-380	3.7-31.8
Pretreatment (Site 2)	.30-1.2	7.5-8.1	2-6	11-24	<.1-.6	<.01-.03	142-187	343-400	2.3-8.6
Post-coagulation (Site 3)	.26-5.2	7.4-8.0	2-6	11-24	<.1-.6	<.01-.02	140-180	345-420	<.15-7.7
Post-filtration (Site 4)	.14-1.3	7.5-8.1	2-5	11-24	<.1-.6	<.01-.02	129-180	346-410	<.15
Post-chlorination (Site 5)	.05-1.3	7.5-8.0	2-5	11-25	<.1-.4	<.01	135-182	346-411	<.15
Simulated Distribution* (Site 5)	.03-1.3	7.6-8.0	2-5	11-25	<.1-.5	<.01	135-183	346-413	<.15

* Held for 24 hours before analysis

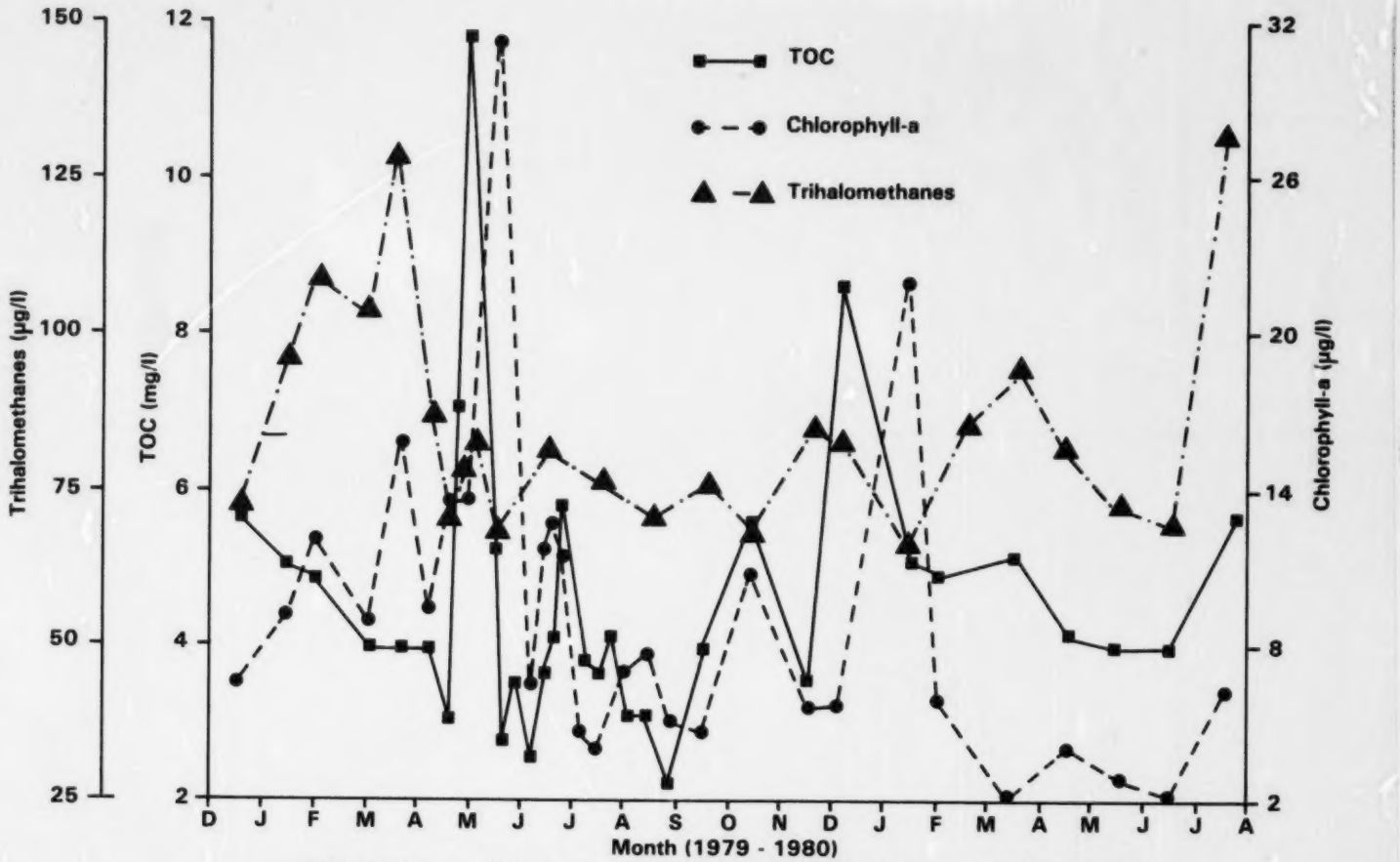

FIGURE 7. Variation in Trihalomethanes Produced and TOC Level at Boerne WTP from December 1979 to August 1980

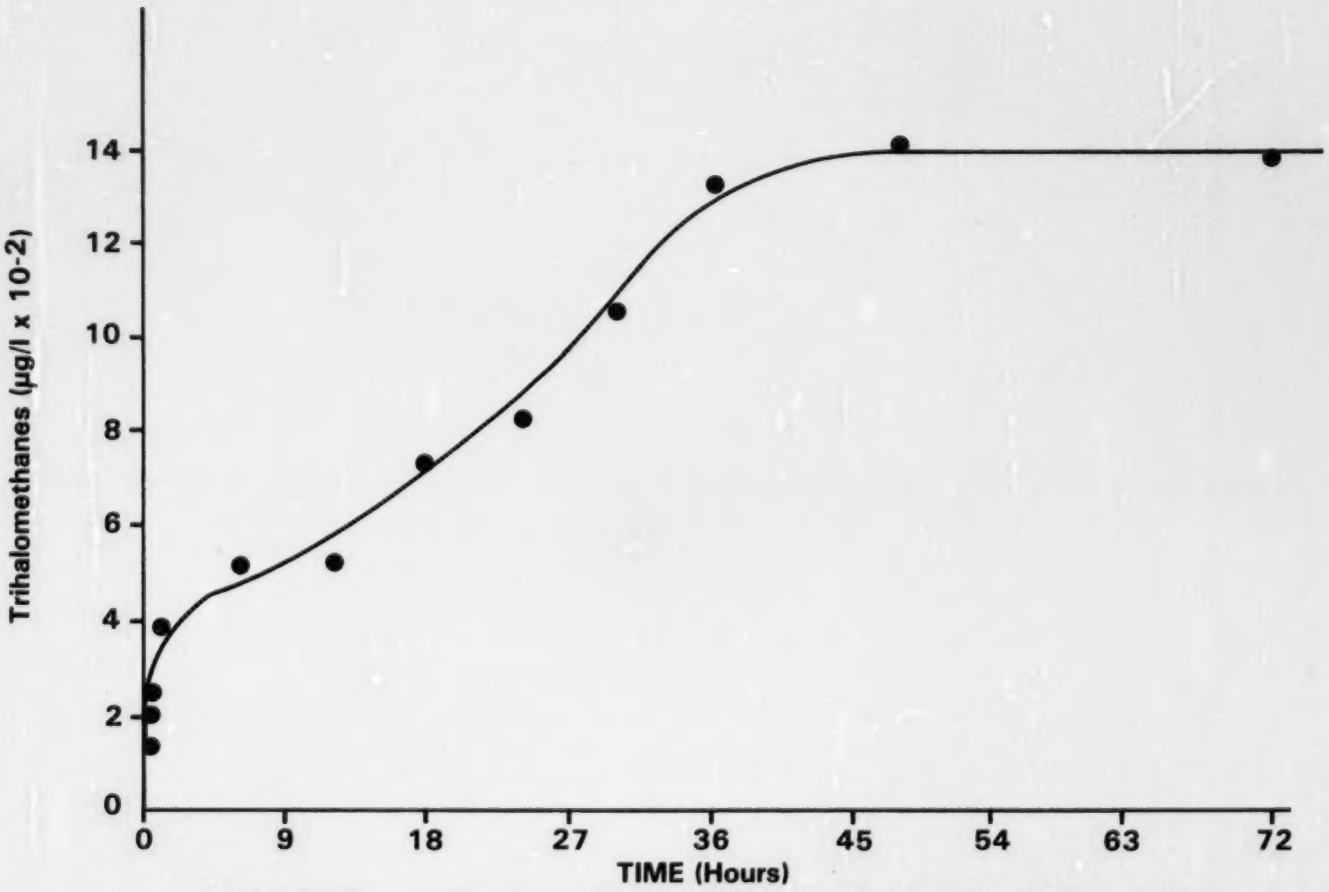

FIGURE 8. Growth Curve of Trihalomethane Production with Time for Boerne WTP

Preliminary Disinfection Studies

Bench-scale experiments were conducted to compare the disinfection response of E. coli lys 147 to a non-lysogenized coliform bacteria, E. coli C. A one liter volume of water obtained at the Boerne WTP was placed in a two liter trypsinizing flask containing a magnetic stirring bar. While rapidly mixing, the test organism was introduced; followed in 10 min by addition of a preselected amount of chlorine. During the disinfection period, samples were removed with a Cornwall© pipetting syringe directly into chilled brain heart infusion broth to quench all residual chlorine.

Representative results for the two coliform bacteria are shown in Figure 9. Both organisms showed typical, biphasic responses to chlorination. Notably, E. coli lys 147 was more sensitive to inactivation by chlorine as demonstrated by a nearly 2 $\log_{10}$ greater reduction at a contact time of 30 min. Nonetheless, this organism was chosen for use in further prototype testing because of the ability to coincidentally monitor the disinfection of indigenous standard plate count (a parameter receiving increasing support as an in-plant measure of disinfection adequacy).

Prototype System

Disinfection --

Disinfection runs with the disinfectant systems shown in Table 11 were performed. All of the disinfection experiments shown are with an organism added to the system. The E. coli lys 147 seed was approximately 2×10^9 pfu/ml and the E. coli C was approximately 3×10^9 cfu/ml.

Figures 10 - 16 graphically depict representative results from disinfection experiments performed using the prototype mixer. The four disinfection schemes presented are described elsewhere (chlorination only, chlorination followed by ammoniation, ammoniation followed by chlorination, and disinfection employing chlorine dioxide). All disinfection data show that both E. coli lys 147 and E. coli C are more susceptible to disinfection than the organisms collectively forming the standard plate count (SPC).

Figure 10 shows bacterial inactivation when chlorine only was employed with the mixer at a dose of 0.5 mg/l. SPC disinfection was not highly significant with less than 99% SPC inactivation being achieved within 1 min. Samples taken at time periods greater than 1 hr appear to substantiate a reestablishment (regrowth) of the SPC population. Greater than 99.999% inactivation of the seeded E. coli lys 147 was achieved in less than 15 sec contact time. Figure 11 depicts the data derived from a chlorination only experiment in which the chlorine dose was 1.5 mg/l. The SPC disinfection test sensitivity of nearly 99% was achieved in 1 min and 99.7% in 24 hr using the 1.5 mg/l chlorine dose; and, greater than 99.999% inactivation of the seeded E. coli lys 147 was achieved within less than 1 sec contact time. Figures 12 and 13 show inactivation of SPC organisms using a chloramination disinfection scheme (the chlorine is injected 15 seconds upstream of ammonia injection and this disinfection scheme is designated herein as CLN) with a 0.5 mg/l and 1.5 mg/l dose, respectively. The 1.5 mg/l dose yielded about 99.5% inactivation of SPC organisms within a 1 min contact time compared to

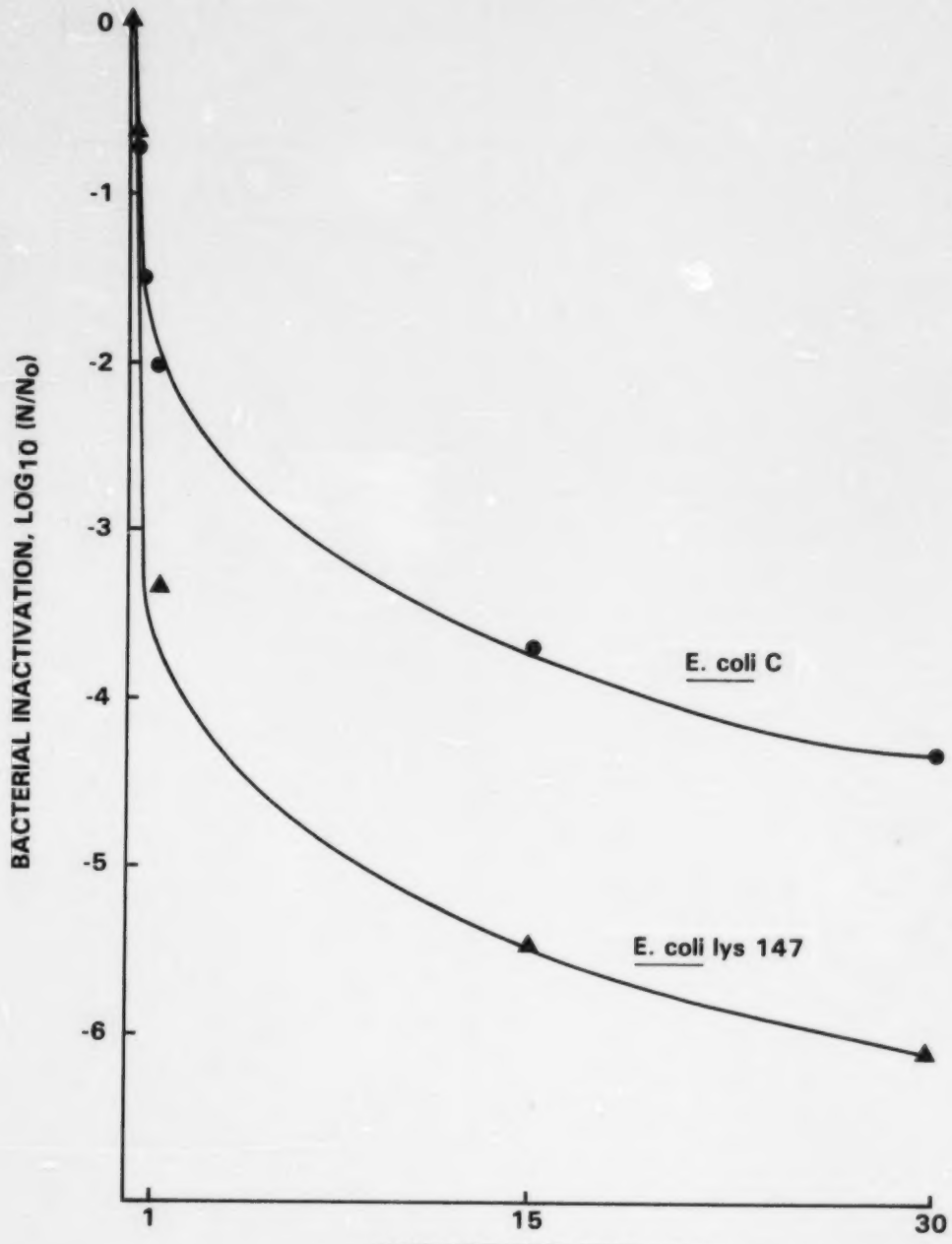

FIGURE 9. Comparative Disinfection of E. coli lys 147 and E. coli C at a Chlorine Dose of 1.2 mg/l

TABLE 11. Disinfection Experiments with the Prototype System

Disinfectant System	Disinfectant Dose (mg/l)	Seed Organism
Chlorine	0.20	*E. coli* lys 147
	0.50	plus *E. coli* C
	1.50	for doses of 0.2
	5.00	and 5.0 mg/l
Chlorine	1.50	Bacteriophage f_2
	5.00	
Ammonia followed by Chlorine	0.50	*E. coli* lys 147
	1.50	plus *E. coli* C
	5.00	
Chlorine followed by Ammonia	0.50	*E. coli* lys 147
	1.50	
	5.00	
Chlorine Dioxide	0.20	*E. coli* lys 147
	0.25	
	0.50	plus *E. coli* C
	1.50	

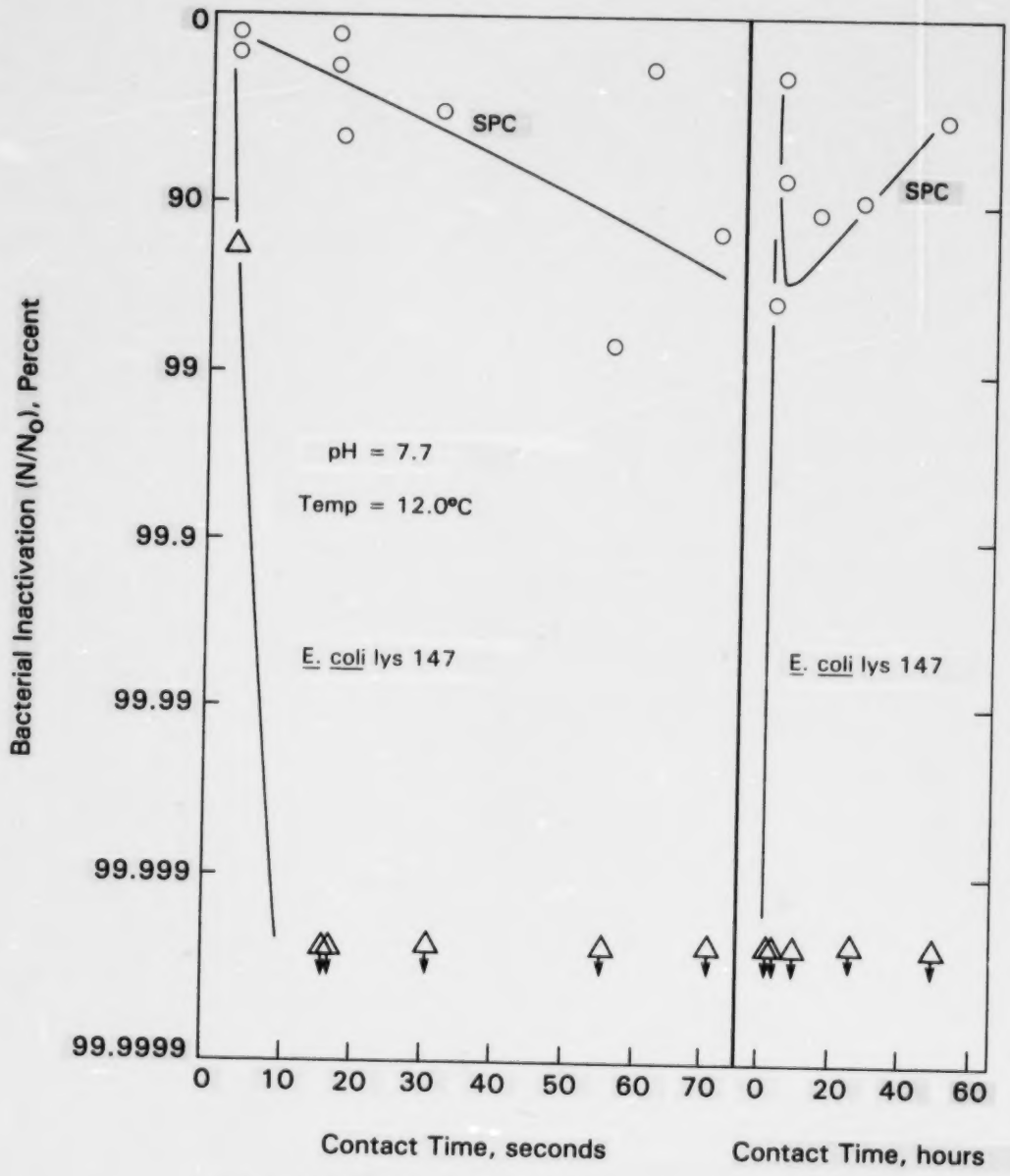

FIGURE 10. Prototype Disinfection Experiment with Chlorine at a Dose of 0.5 mg/l

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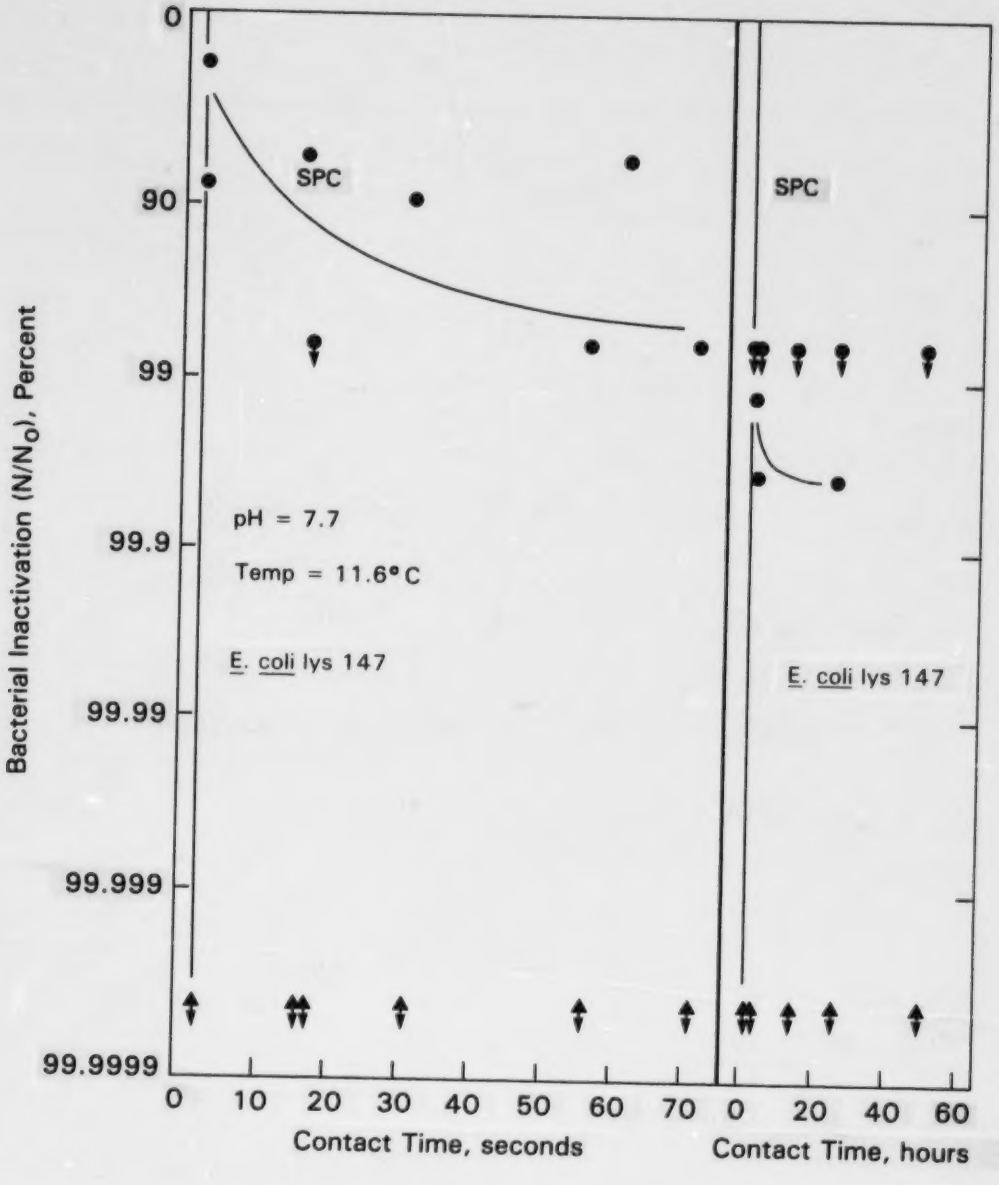

FIGURE 11. Prototype Disinfection Experiment with Chlorine at a Dose of 1.5 mg/l

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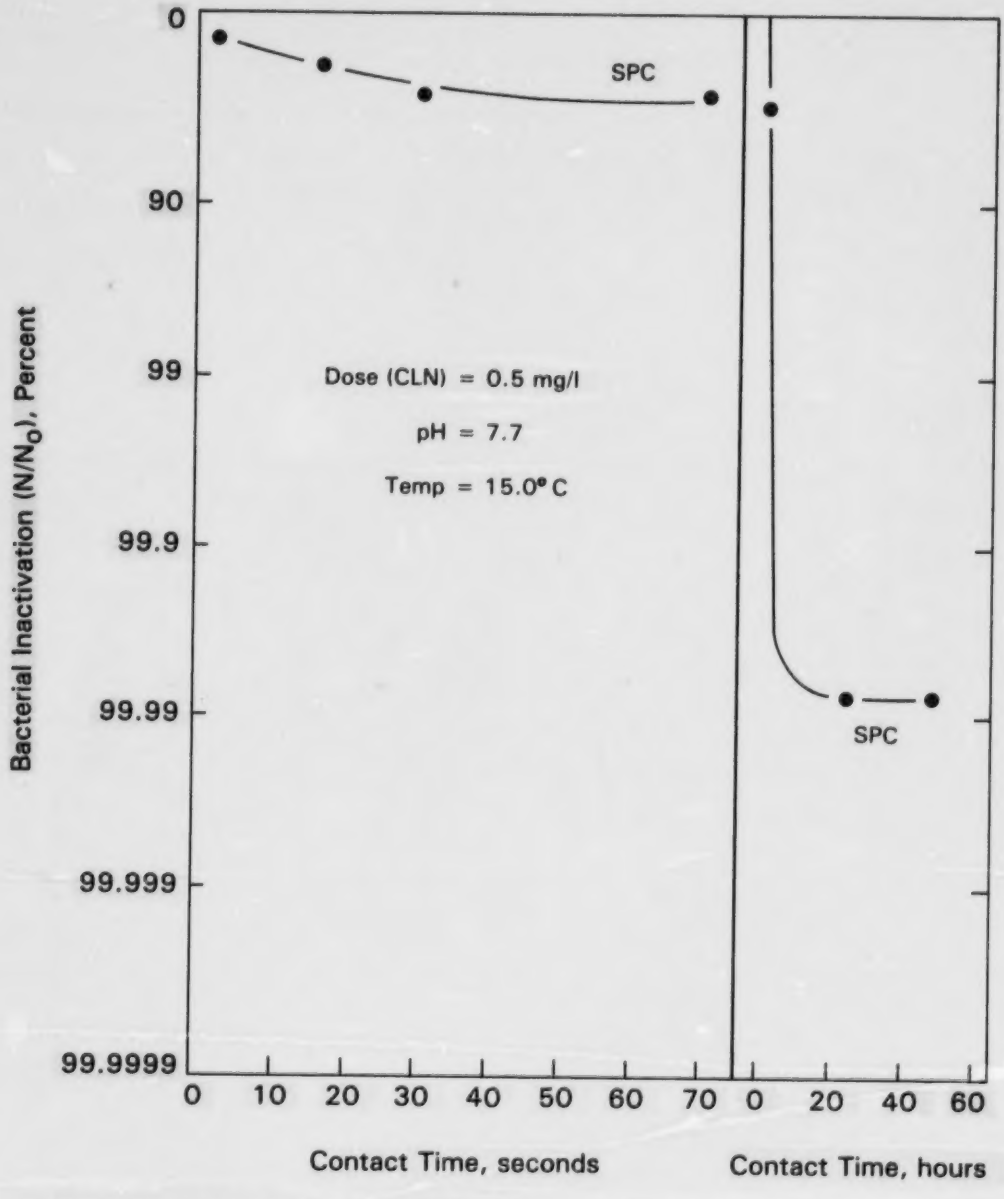

FIGURE 12. Prototype Disinfection Experiment with Chlorine Followed by a Gravimetric Equivalent of Ammonia after 15 Seconds of Contact Time

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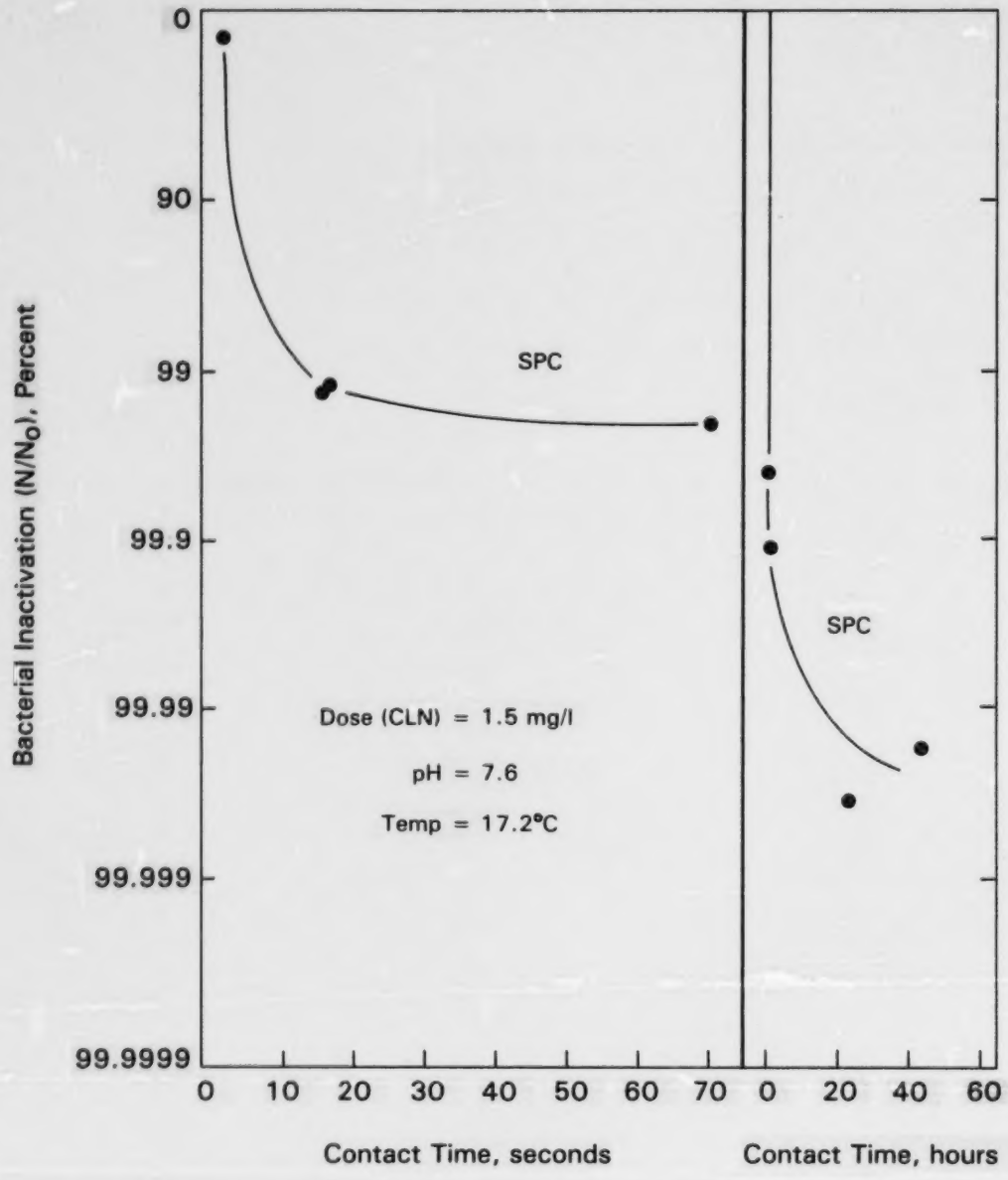

FIGURE 13. Prototype Disinfection Experiment with Chlorine Followed by a Gravimetric Equivalent of Ammonia after 15 Seconds of Contact Time

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a 55% inactivation with the 0.5 mg/l dose. However, after 24 hr contact time the inactivation of SPC organisms was similar: 99.993% for a dose of 1.5 mg/l relative to 99.98% for a dose of 0.5 mg/l. When compared to the disinfectin scheme using chlorine alone (Figures 10 and 11), the CLN disinfection scheme using doses of 0.5 and 1.5 mg/l, was markedly superior for SPC organisms at sustained contact times.

Figure 14 depicts the inactivation of SPC organisms and E. coli lys 147 for a chlorine dose of 5.0 mg/l and a corresponding gravimetric ammonia dose. In one experiment the ammonia was injected approximately 15 sec flowtime upstream of the chlorine injection point (NCL); and, in a second experiment, the ammonia was injected approximately 15 sec flowtime downstream of the chlorine injection point (CLN). In both experiments (CLN and NCL), the E. coli lys 147 population experienced a reduction greater than 99.999% in 1 sec or less. The SPC organism population was not nearly as susceptible to disinfection and, at a 5.0 mg/l chlorine dose, no significant difference existed between the SPC organism populations subjected to the CLN or NCL disinfection schemes. These organisms experiencd an approximate 99% reduction nearly instantaneously; and, the inactivation of the SPC organisms proceeded to a reduction of about 99.99% after 24 hr contact time.

Figure 15 shows disinfection results for SPC organisms obtained in a single experiment using chlorine dioxide as the disinfectant at doses of 0.235, 0.390, and 1.49 mg/l. The solid line represents inactivation of SPC organisms (90% inactivation in 1 min) for a dose of 0.235 mg/l while the dashed line approximates inactivation for the other two doses. Dta at the 15 sec and 71 sec times for doses of 0.390 and 1.490 are anomalous based on other chlorine dioxide runs. The sample vials used for these dta points may have been contaminated. After 24 hr contact time, 99.3% inactivation was achieved with the 0.135 mg/l ClO_2 dose, and greater than 99.8% inactivation was achieved with the 0.390 and 1.49 mg/l doses. Figure 16 depicts a single experiment in which 0.25 mg/l doses of chlorine dioxide and chlorine alone were compared for their efficacy as disinfectants. Chlorine dioxide was the superior disinfectant for SPC organisms achieving approximately 98.8% inactivation in 1 min compared to only 55% for chlorine. After 1 hr contact time the inactivation achieved by chlorine dioxide remained at 98% while chlorine inactivation of the SPC organisms increased to 98%. Both disinfectants reduced E. coli lys 147 populations by greater than 99.999% in approximately 20 sec.

The relationship between disinfectant residual and SPC organism inactivation was evaluated relative to the residual's interaction with contact time. Three models (equations 14-16) were developed to express the residualcontact time relationship. When chlorine or chlorine plus ammonia were used in the disinfection scheme, the data were fit to the models separately using both free and total residuals.

$$\text{Model A:} \quad y = b_o R^{b_1} t \tag{14}$$

$$\text{Model B:} \quad y = b_o (Rt)^{b_1} \tag{15}$$

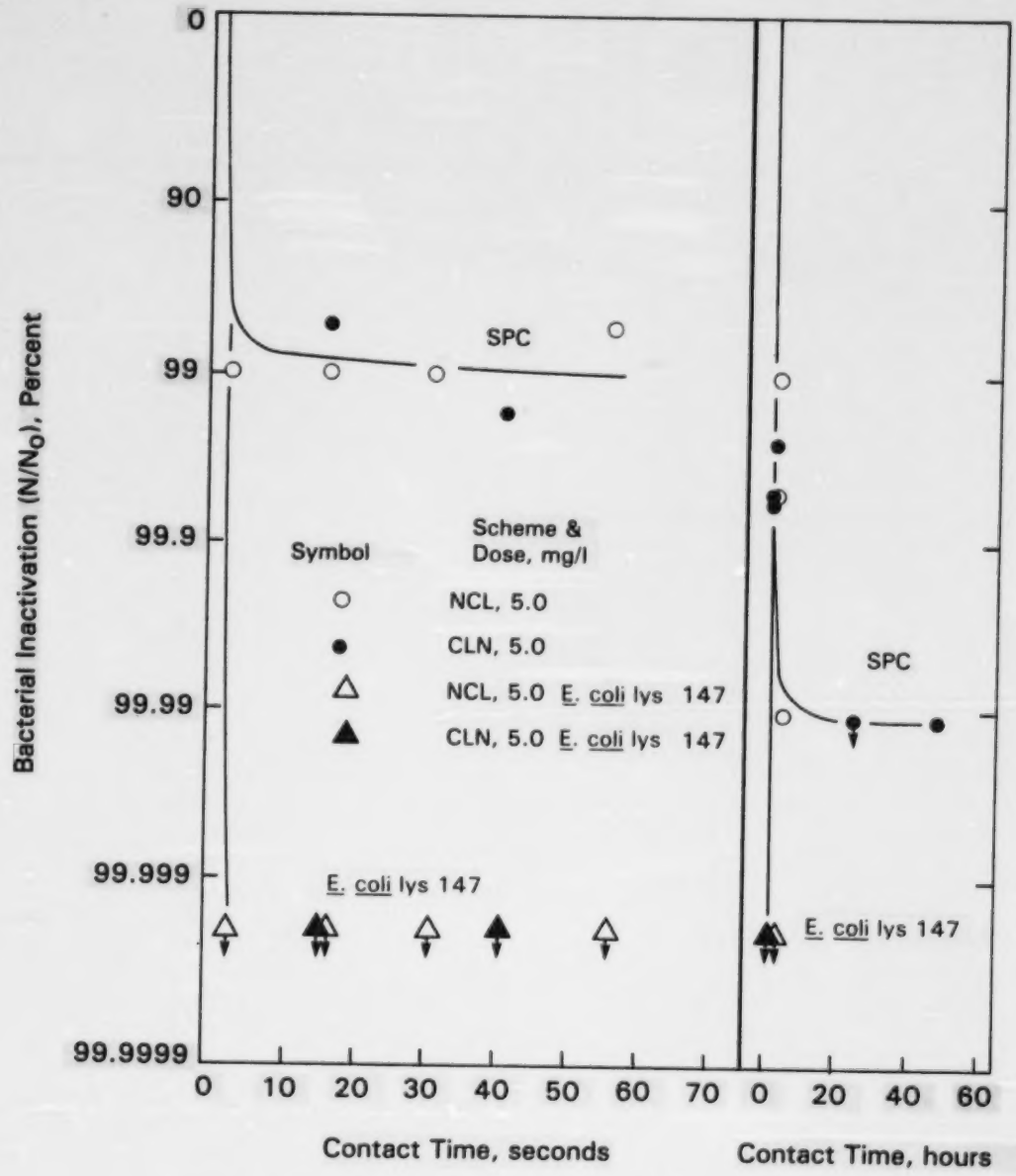

FIGURE 14. Prototype Disinfection Experiments with Chlorine Followed by Ammonia (CLN) and Ammonia Followed by Chlorine (NCL). All Doses were Gravimetrically Equivalent at 5.0 mg/l and the Contact Time Before Addition of the Second Component was 15 Seconds.

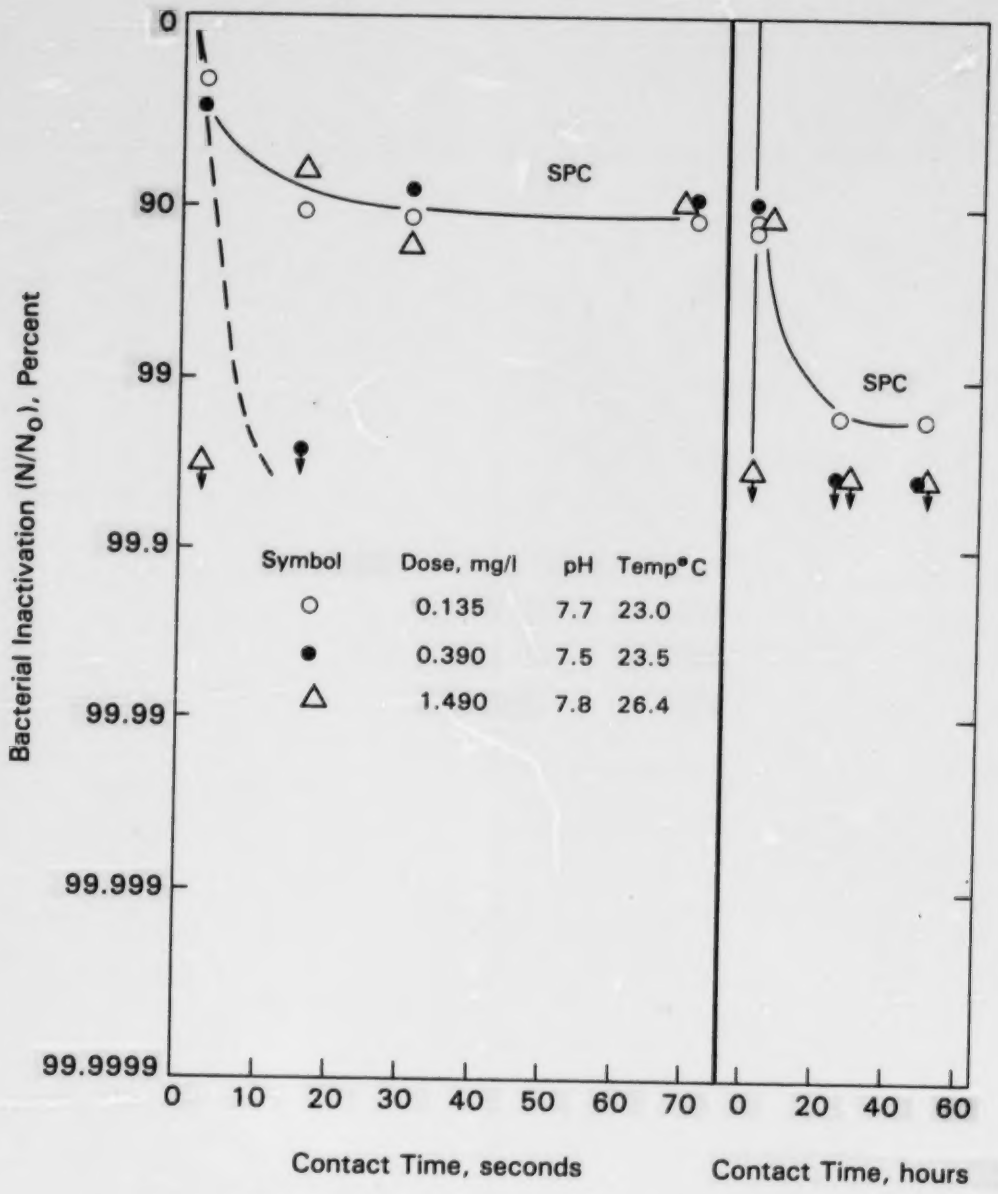

FIGURE 15. Prototype Disinfection Experiments with Chlorine Dioxide at Three Doses

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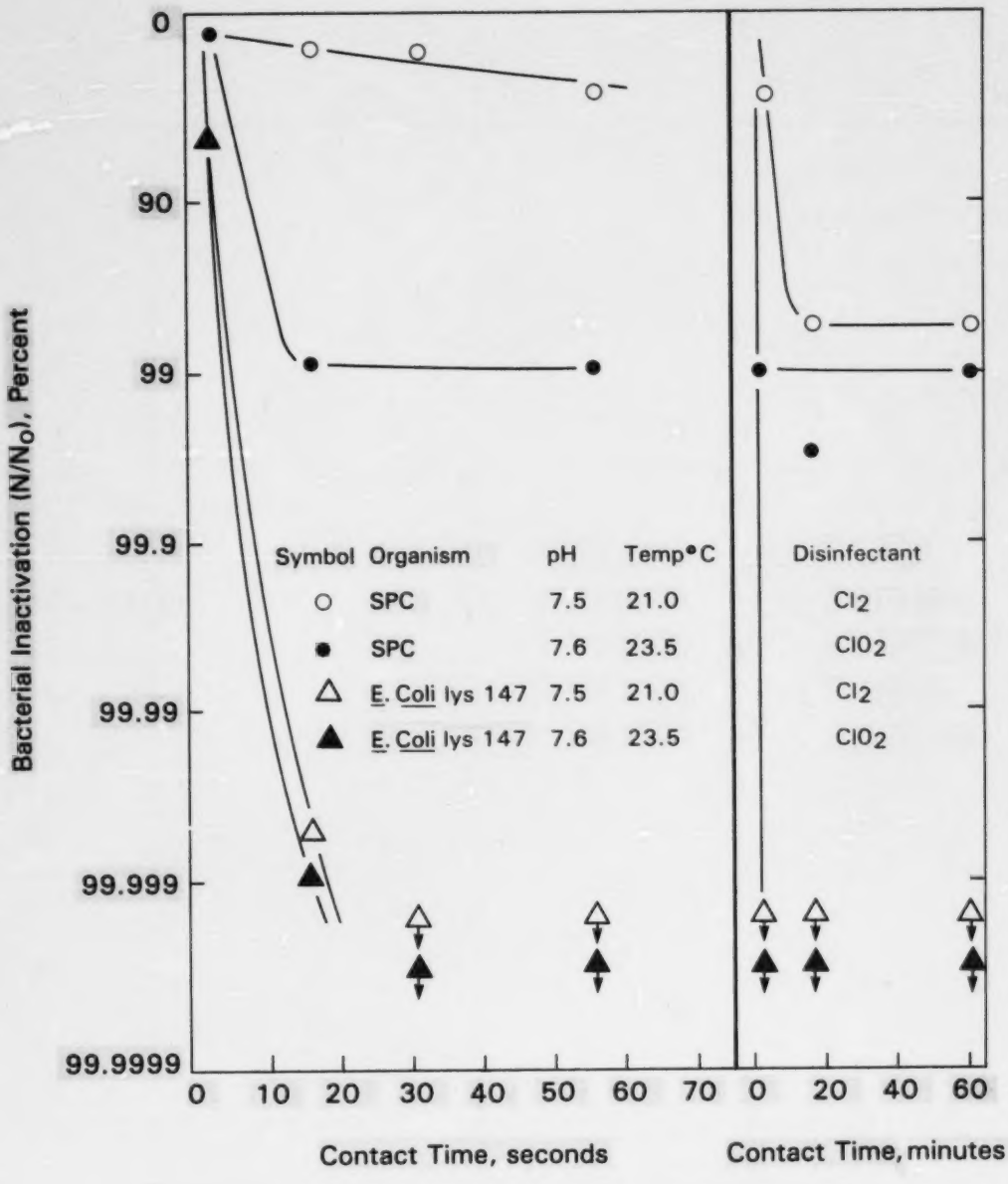

FIGURE 16. Prototype Disinfection Experiments with a 0.25 mg/l Dose of Chlorine Dioxide Compared to a 0.25 mg/l Dose of Chlorine.

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Model C: $y = b_o R^{b_1} t^{b_2}$ (16)

where: R = disinfectant residual at time zero, mg/l
t = contact time, sec
y = survival fraction of SPC organisms
b_o, b_1, b_2 = regression coefficients

The statistics for the above models are shown in Table 12. Model A does not describe the experimental data. However, Models B and C both provide significant descriptions of the experimental data as shown by associated correlation coefficients and Fisher (F) test values. The correlation coefficient and Fisher test value are both directly related to error in model fit; however, both are shown for convenience. For those experiments where chlorine or chloramination was employed, Model B appears to be superior to Model C since the expression, $(Rt)^{b_1}$, describes 40% to 63% of "y"; whereas, the expression, $R^{b_1}t^{b_2}$, associated with Model C describes only 16% to 40% of "y".

Figures 17 through 21 depict Models B and C shown together with actual disinfection data. The residual (R) values on these figures refer to disinfectant residuals. Actual disinfection data are referenced to disinfectant dose for convenience since the total residual corresponded to dose for contact times of 1 hr and less. Figures 17 and 18 show the application of free and total chlorine residual data, respectively, to Models B and C where chlorine only was used as the disinfectant. Since the free and total residuals were nearly identical in all cases (little or no chloramines), the results depicted in Figures 17 and 18 are nearly identical. Model B and Model C_1 (where R = 0.5 mg/l) express essentially the same curve which visually provides a good data fit. Model C_2 (where R = 5.0 mg/l), however, provides an overestimation of disinfection efficiency.

The application of Models B and C to chloramination (chlorine injection followed 15 sec downstream by ammonia injection) data is depicted graphically in Figures 19 and 20 for free and total residual data, respectively. Model B, when applied to both free and total residual data, overestimated disinfection efficiency for 0.5 mg/l chlorine dose data and underestimates disinfection efficacy for 5.0 mg/l chlorine dose data. It is apparent that both the free residual and the total residual data fall into two distinct data groups depending upon the concentration of the disinfectant. Consequently Model B does not represent either group. Model C_1 (R = 0.5 mg/l) overestimates disinfection efficiency using free residual data, and underestimates disinfection efficiency using total residual data. However, Model C_2 (R = 5.0 mg/l) provides a good fit with the observed data.

Models B, C_1 (R = 0.14 mg/l), and C_2 (R = 1.49 mg/l), shown in Figure 21, describe the same curve which is an adequate fit of actual disinfection data obtained using chlorine dioxide as the disinfectant and SPC organisms.

A disinfection experiment with a virus seed, bacteriophage f2, was performed at two chlorine doses as shown in Table 13. At the low chlorine dose, 1.5 mg/l, disinfection of the phage or the indigenous organisms (SPC) was accomplished effectively within one min and 15 sec of contact

TABLE 12. Statistics Summary for Disinfection Models

Data Source+	Model Number	Regression Coefficients b_o	b_1	b_2	Correlation Coefficient r(R)	Fisher Test F
Cl_2:FAC	A	3.66×10^{-3}	6.223	--	0.163	0.527
Cl_2:TAC	A	2.90×10^{-3}	0.477	--	0.114	0.250
CLN:FAC	A	9.10×10^{-4}	-1.114	--	-0.430	2.043
CLN:TAC	A	5.26×10^{-3}	-2.681	--	-0.649*	6.544*
ClO_2	A	7.50×10^{-3}	1.659	--	0.279	1.353
Cl_2:FAC	B	0.629	-0.301	--	-0.587**	9.443**
Cl_2:TAC	B	0.590	-0.275	--	-0.558*	8.117*
CLN:TAC	B	0.447	-0.588	--	-0.744**	11.179**
CLN:TAC	B	0.432	-0.481	--	-0.611*	5.356*
ClO_2	B	0.214	-0.280	--	-0.623**	10.139**
Cl_2:FAC	C	0.398	-0.849	-0.277	0.731**	9.749**
Cl_2:TAC	C	0.376	-0.870	-0.240	0.693**	8.056**
CLN:FAC	C	0.163	-1.323	-0.357	0.943**	31.957**
CLN:TAC	C	0.354	-2.219	-0.165	0.981**	102.606**
ClO_2	C	0.222	-0.241	-0.278	0.673*	4.757*

* 95% level; ** 99% level

\+ Disinfectant Systems: Cl_2 - chlorine only; CLN - Chlorine followed by Ammonia; ClO_2 - chlorine dioxide
Residual Chlorine: FAC - Free available chlorine; TAC - total available chlorine

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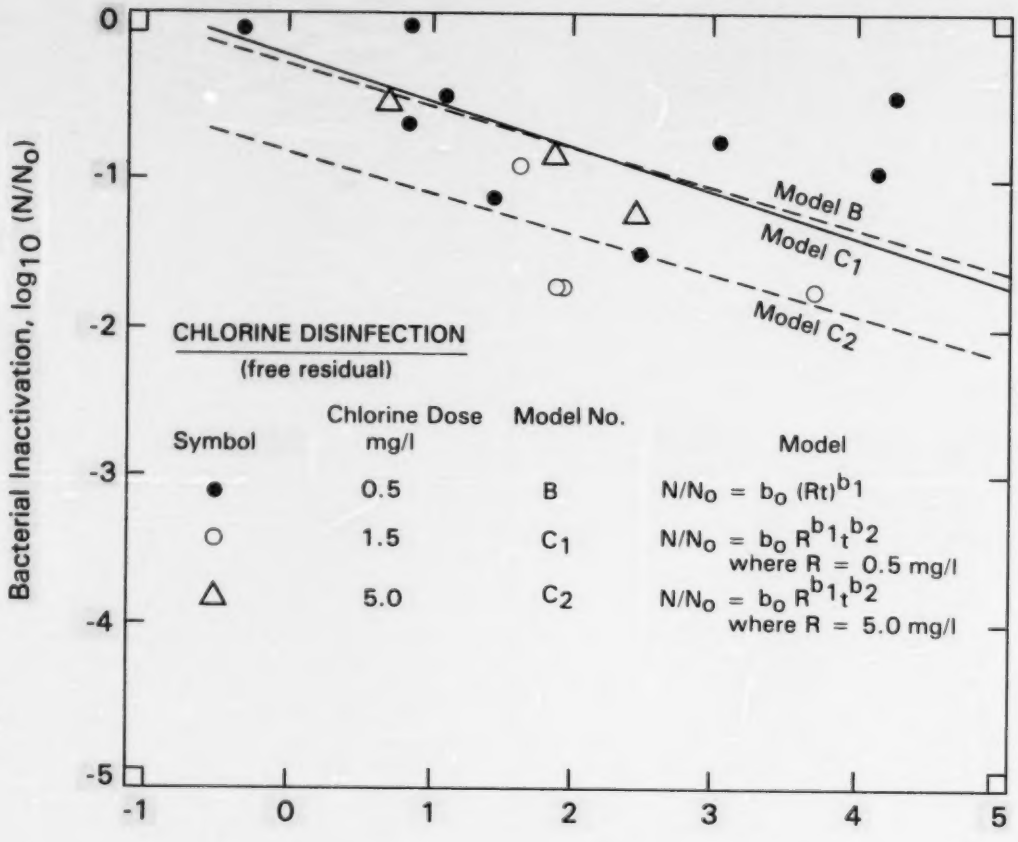

FIGURE 17. Bacterial Inactivation (SPC) as a Function of Free Residual - Contact Time Product for Chlorine Disinfection

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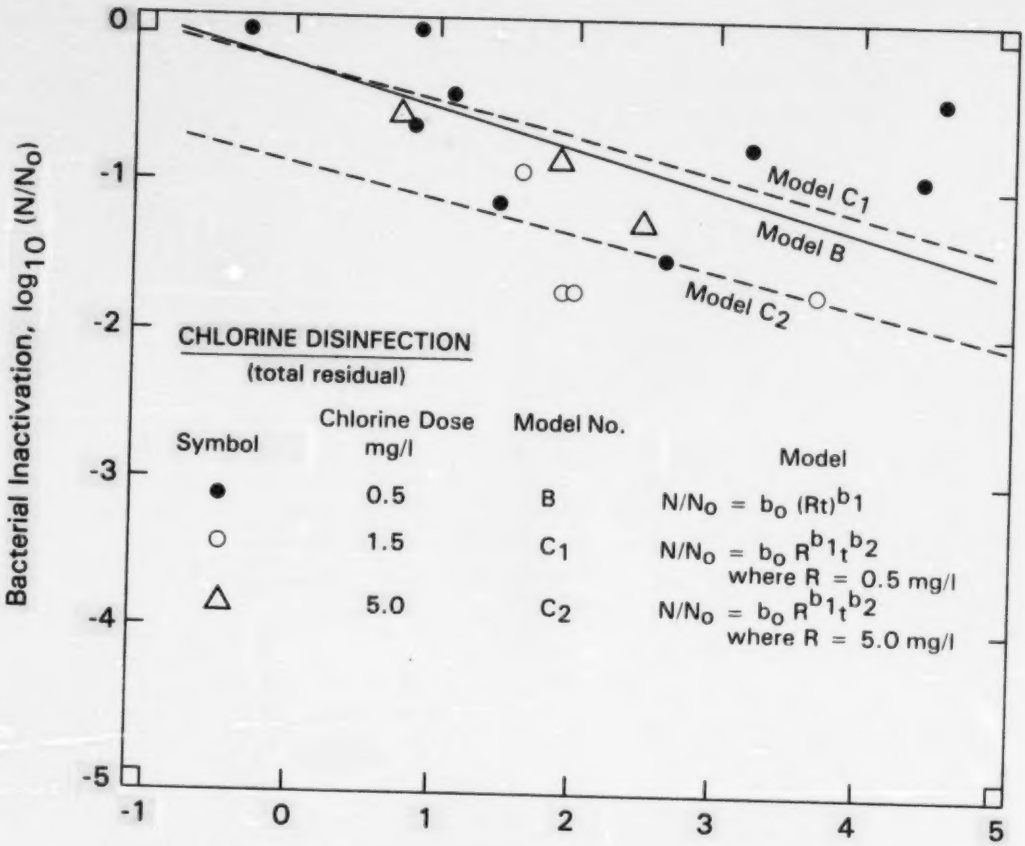


FIGURE 18. Bacterial Inactivation (SPC) as a Function of Total Residual - Contact Time Product for Chlorine Disinfection

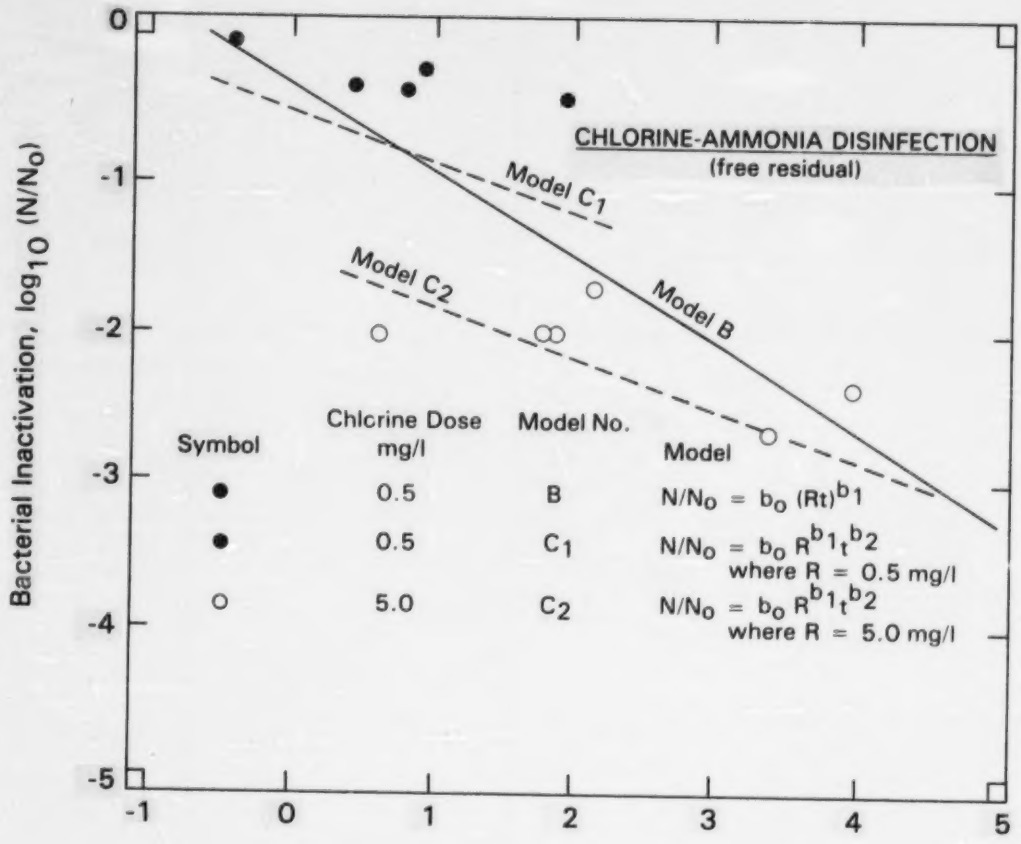
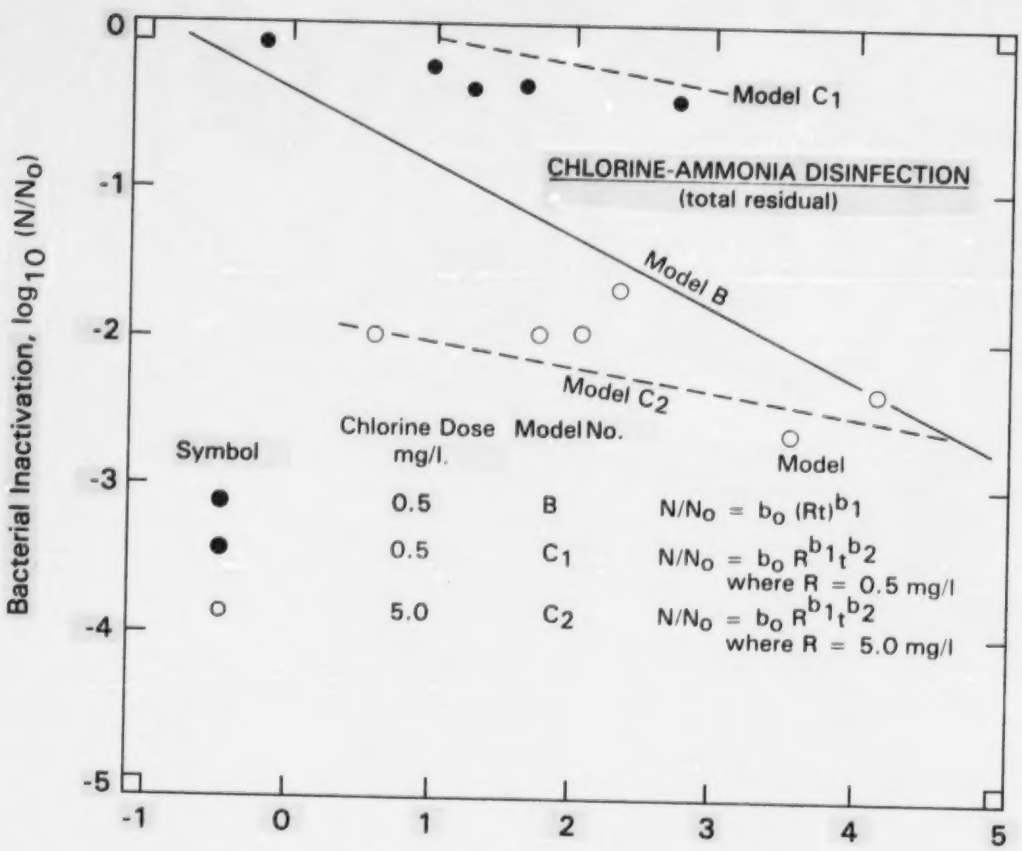


FIGURE 19. Bacterial Inactivation (SPC) as a Function of Free Residual - Contact Time Product for Chlorine Followed by Ammonia Disinfection



Residual - Contact Time Product, log (Rt), mg/l/sec

FIGURE 20. Bacterial Inactivation (SPC) as a Function of Total Residual - Contact Time Product for Chlorine Followed by Ammonia Disinfection

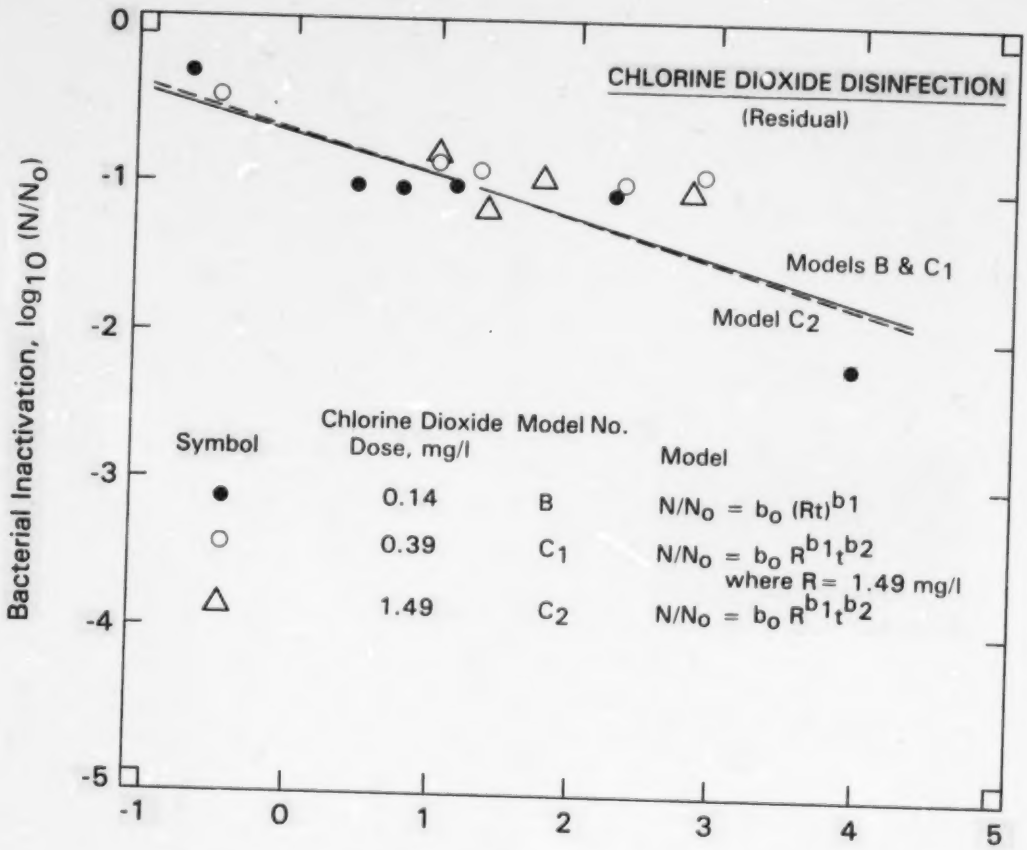


FIGURE 21. Bacterial Inactivation (SPC) as a Function of Residual - Contact Time Product for Chlorine Dioxide Disinfection

TABLE 13. Disinfection of Bacteriophage f_2 by the Prototype System with Chlorine as Disinfectant

Chlorine Dose mg/l	Contact Time	Bacteriophage f2 pfu/ml	Standard Plate Count, cfu/ml
1.5	0	$<6.7 \times 10^{-1}$	7.7×10^{2}
	0*	4.2×10^{6}	4.3×10^{2}
	1 sec	8.0×10^{5}	1.6×10^{1}
	15 sec	1.8×10^{5}	3.3×10^{0}
	31 sec	8.0×10^{3}	6.0×10^{0}
	56 sec	6.7×10^{-1}	3.0×10^{0}
	15 min	$<6.7 \times 10^{-1}$	2.3×10^{0}
	1 hr	$<6.7 \times 10^{-1}$	6.7×10^{-1}
	24 hr	$<6.7 \times 10^{-1}$	3.3×10^{-1}
5.0	0	$<6.7 \times 10^{-1}$	9.8×10^{2}
	0*	5.5×10^{6}	8.5×10^{2}
	1 sec	1.4×10^{4}	8.7×10^{0}
	15 sec	1.7×10^{3}	3.0×10^{0}
	21 sec	$<6.7 \times 10^{-1}$	6.7×10^{-1}
	56 sec	$<6.7 \times 10^{-1}$	1.0×10^{0}
	15 min	$<6.7 \times 10^{-1}$	$<3.3 \times 10^{-1}$
	1 hr	$<6.7 \times 10^{-1}$	$<3.3 \times 10^{-1}$
	24 hr	$<6.7 \times 10^{-1}$	$<3.3 \times 10^{-1}$

* After addition of bacteriophage f_2 (seeded unchlorinated control)

time, respectively. At the higher chlorine dose, 5.0 mg/l, the phage was inactivated within 30 sec and the SPC was eliminated within one sec of contact time.

Chemical Parameters --

The same chemical parameters that were determined for the normal operation of the WTP were determined for the prototype operation. Regardless of disinfectant system or dose there were no substantial differences between the values otained for the prototype system and those obtained for the WTP. Table 14 shows a typical set of chemical parameters and values obtained for the operation of the prototype system with three doses of chlorine as the disinfectant. When the prototype was operated with the disinfection systems containing ammonia, the NH_3 levels and pH values were slightly elevated.

The only chemical parameter that has been significantly affected by operation of the prototype system compared to the WTP is trihalomethane production. Tables 15 and 16 show two typical runs obtained from operation of the prototype system with chlorine as the disinfectant. Comparison of the THM values with those observed for the normal plant operation show lower overall values for the prototype system. Figures 22 - 25 show similar results for the chlorine followed by ammonia, ammonia followed by chlorine, chlorine dioxide, and chlorine (lowest effective disinfectant dose) disinfectant systems. In all cases effective disinfection has occurred and reduced terminal THM are observed.

Figures 22 and 23 represent the production of THM in the presence of chloramines. In contrast to the chlorine dioxide run (Figure 24), which showed no increase in THM levels after a minute, both experiments where ammonia was added after or before the chlorine showed an increase in TTHM produced. The reaction of chlorine with ammonia and the THM precursors in the water is a competitive process; therefore, intermediates which break down more slowly to THM may be formed giving rise to the slow increase in THM. For the addition of ammonia after chlorine the level increased four-fold from 3 µg/l at 1 min to a terminal value of approximately 13 µg/l. This represents 50% of the THMFP of the water at a dose of 0.5 mg/l. The prototype run with ammonia added before chlorine produced fewer intermediates that react slowly because of a more favorable interaction with the ammonia already present. The two-fold increase of 6 µg/l at 1 min to a terminal value of approximately 11 µg/l was very modest. Furthermore this level of THM production represents only 20% of the THMFP of the water at a dose of 1.5 µg/l. The addition of ammonia clearly precluded achieving the THMFP of the water; however, the small increases were likely caused by the interaction of the rapid mixing system with THM precursors giving rise to some intermediates that break down slowly with time to THM. Alternatively, if only the chloroform values were plotted there was essentially no increase after one minute (see Table 17).

As with disinfection several models were examined for THM production. The model best expressing THM production relative to time and chlorine residual is given by equation 17.

$$Z = b_o\left(\sum_{i=1}^{M} R_i t_i\right)^{b_1} \qquad (17)$$

TABLE 14. Chemical Parameters Obtained for Prototype Operation with Chlorine as Disinfectant

Sampling Time	Chlorine Dose (mg/l)	Total Chlorine Residual (mg/l)	Turbidity (NTU)	pH	TOC (mg/l)	TKN (mg N/l)	NH_3 (mg N/l)	Total Alkalinity (mg/l $CaCO_3$)	Specific Conductivity (μmhos/cm)	Temperature °C
0	0.50	0.00	0.17	7.80	5	0.20	0.01	209	460	12
1 sec		0.56	0.24	7.80	6	0.50	0.02	198	460	13
1 min		0.35	0.17	7.75	5	0.40	0.02	194	460	13
15 min		0.26	0.15	7.85	5	0.40	0.02	189	460	13
60 min		0.26	0.21	7.90	6	0.70	0.02	196	460	16
0	1.50	0.0	0.23	7.90	6	0.10	0.02	196	460	12
1 sec		1.20	0.17	7.85	5	0.70	0.02	202	460	13
1 min		1.03	0.12	7.90	4	0.70	0.02	202	460	13
15 min		0.70	0.20	7.95	5	0.50	0.02	198	460	14
60 min		0.70	0.19	7.90	5	0.50	0.02	198	460	15
0	5.0	0.00	0.20	7.90	5	0.30	0.02	200	448	13
1 sec		5.58	0.25	7.70	5	0.40	0.02	198	454	12
1 min		5.00	0.22	7.80	5	0.30	0.02	200	460	13
15 min		4.90	0.22	7.80	6	0.60	0.01	196	460	13
60 min		4.75	0.39	7.80	5	0.60	0.02	196	454	13

TABLE 15. Formation of Trihalomethanes During Operation of the Prototype System with Chlorine as Disinfectant (Run 1)

Chlorine Dose (mg/l)	Contact Time	Total Cl_2 Residual	Free Cl_2 Residual	$CHCl_3$ µg/l	$CHCl_2Br_2$ µg/l	$CHClBr_2$ µg/l	THM* µg/l	THM+ µg/l
0.50	0 sec	0.00	0.00	<0.10	<0.10	<0.10	<0.10	<0.10
	1 sec	0.43	0.31	<0.10	0.24	<0.10	0.24	0.24
	15 sec	0.41	0.26	5.44	0.07	1.34	5.51	6.85
	55 sec	0.34	0.21	7.08	0.42	0.36	7.50	7.86
	15 min	0.19	0.12	7.13	1.69	2.86	8.82	11.68
	60 min	0.18	0.09	5.96	1.25	<0.10	7.21	7.21
	12 hr	-	-	6.79	1.72	<0.10	8.51	8.51
	24 hr	0.15	0.03	7.91	2.21	0.45	10.12	10.57
	48 hr	-	0.03	8.97	1.86	0.75	10.83	11.58
	72 hr	0.10	0.03	10.14	2.37	2.12	12.51	14.63
	Terminal	0.10	0.03	10.28	2.21	2.34	12.49	14.83
1.50	0 sec	0.00	0.00	<0.10	<0.10	<0.10	<0.10	<0.10
	1 sec	1.65	1.43	<0.10	<0.10	<0.10	<0.10	<0.10
	55 sec	1.65	1.37	3.55	0.53	2.53	4.08	6.61
	15 min	1.15	1.01	4.90	3.57	2.85	8.47	11.32
	60 min	0.96	0.73	7.91	6.23	2.72	14.14	21.86
	12 hr	-	-	14.40	12.47	5.80	26.87	32.67
	24 hr	0.87	0.60	18.78	14.05	5.87	32.83	38.70
	48 hr	-	0.58	19.99	15.52	6.60	35.51	42.11
	72 hr	0.75	0.56	21.12	17.06	7.56	38.18	45.74
	Terminal	0.63	0.53	22.61	18.36	9.71	40.97	50.68
5.00	0 sec	0.00	0.00	<0.10	<0.10	<0.10	<0.10	<0.10
	1 sec	5.00	4.52	<0.10	<0.10	<0.10	<0.10	<0.10
	55 sec	5.00	4.44	6.29	1.07	0.10	7.36	7.46
	15 min	4.60	3.92	8.69	5.84	0.74	14.53	15.27
	60 min	4.30	3.64	16.51	9.49	0.45	26.00	26.45
	12 hr	-	-	29.80	15.61	<0.10	45.41	45.41
	24 hr	4.05	2.68	52.46	30.18	5.84	82.64	88.48
	48 hr	-	2.52	53.41	25.94	1.08	79.35	80.43
	72 hr	3.92	2.12	137.90	41.48	5.56	179.38	184.94
	Terminal	3.85	2.01	152.02	48.61	9.09	200.63	209.72

* THM as $CHCl_3$ + $CHCl_2Br$ only
\+ Total THM

TABLE 16. Formation of Chloroform During Operation of the Prototype System with Chlorine as Disinfectant (Run 2)

Sampling Time	Chlorine Dose (mg/l)	Instantaneous Chloroform InstTHM (μg/l)	Terminal Chloroform (μg/l)
0	0.5	>0.1	>0.1
1 sec		>0.1	6.3
1 min		1.7	7.1
15 min		3.1	6.2
60 min		4.3	8.1
0	1.5	>0.1	>0.1
1 sec		>0.1	28.9
1 min		2.8	27.6
15 min		5.1	24.3
60 min		9.3	29.4
0	5.0	>0.1	>0.1
1 sec		0.3	98.7
1 min		3.9	96.4
15 min		7.1	95.8
60 min		21.7	100.0

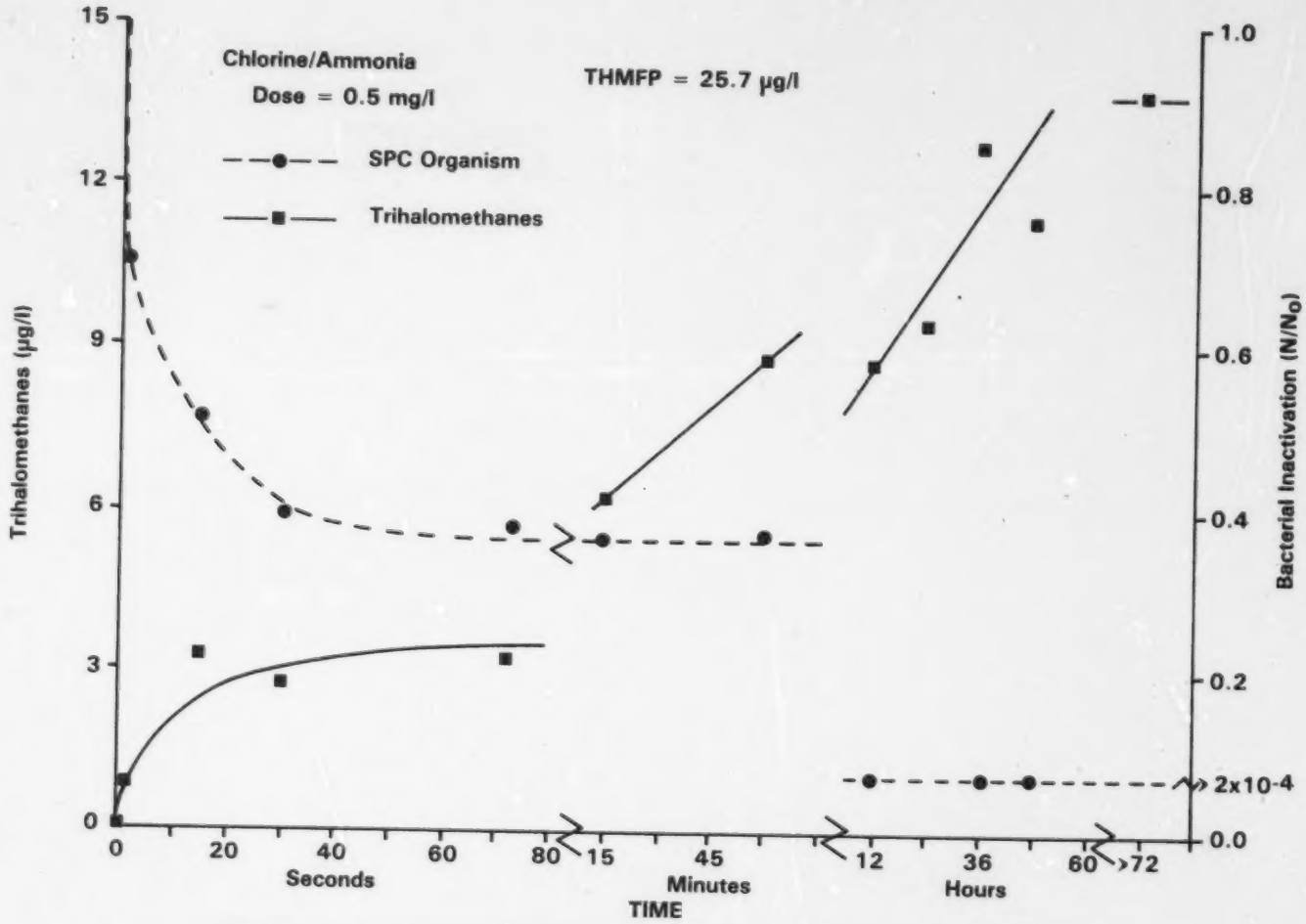


FIGURE 22. Production of Trihalomethanes with Time for Prototype Disinfection by Chlorine Followed by Ammonia

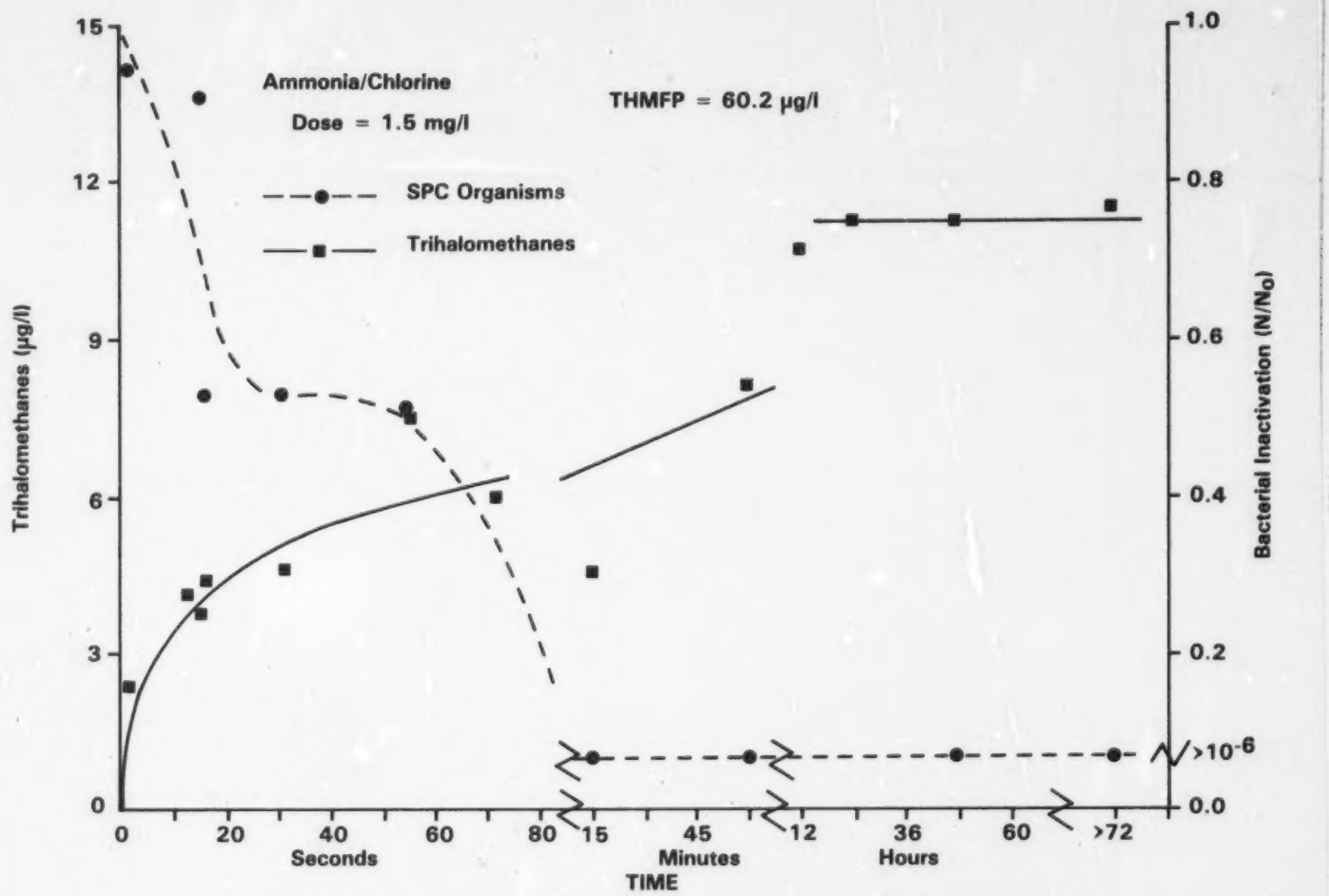


FIGURE 23. Production of Trihalomethanes with Time for Prototype Disinfection by Ammonia Followed by Chlorine

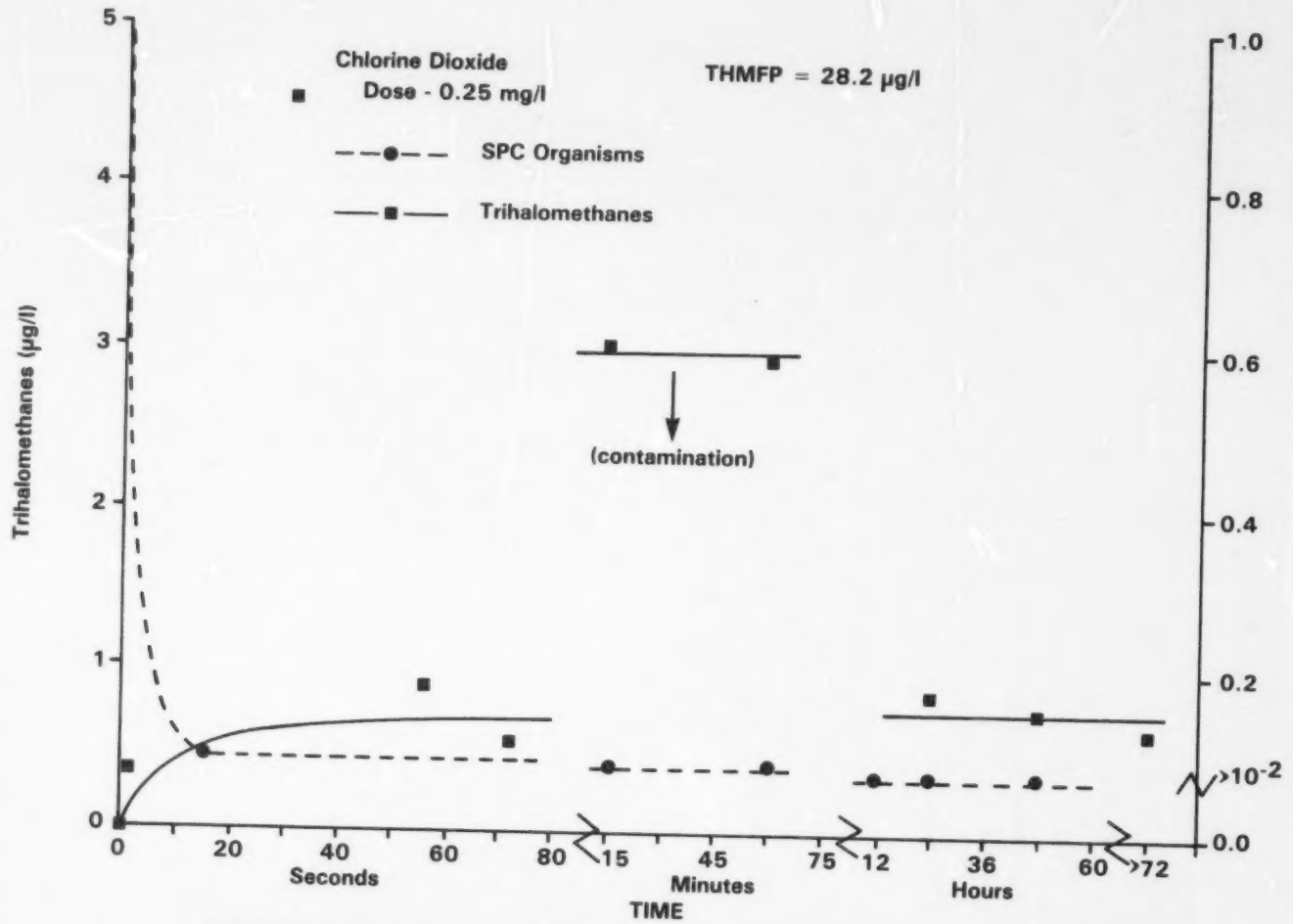


FIGURE 24. Production of Trihalomethanes with Time for Prototype Disinfection by Chlorine Dioxide

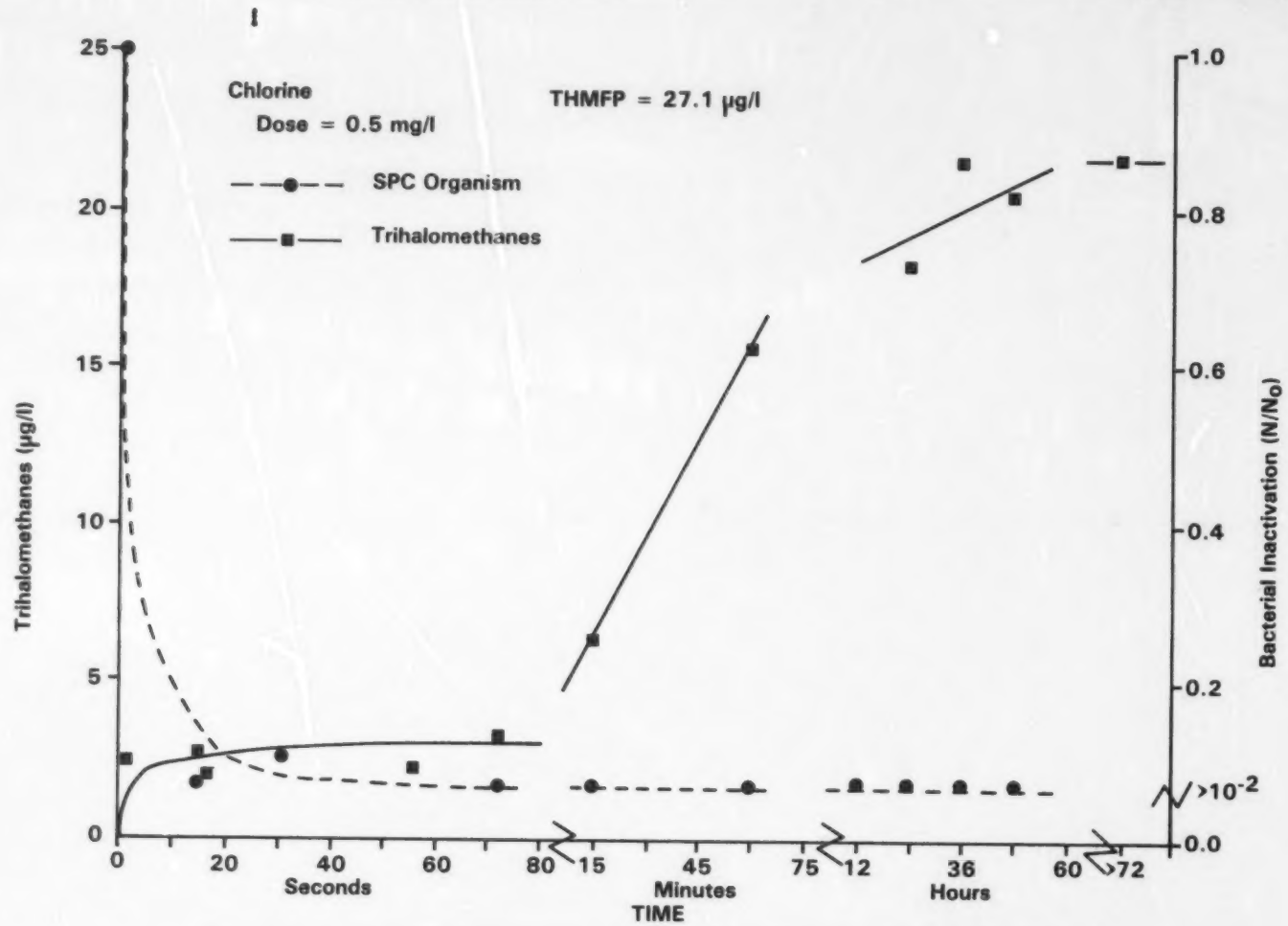


FIGURE 25. Production of Trihalomethanes with Time for Prototype Disinfection by Chlorine

TABLE 17. Trihalomethane Production from Several Disinfectant Systems

Disinfectant Dose (mg/l)	Disinfectant System	THM Production (µg/l)				
		$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHM
0.00	None	<0.1	<0.1	<0.1	<0.1	<0.1
0.25	Chlorine	1.06	1.80	1.43	<0.1	4.29
	Chlorine Dioxide+	0.24	0.11	<0.1	<0.1	0.35
0.50	Chlorine	1.87	2.17	1.18	1.07	6.29
		4.17	6.46+	8.22+	2.42+	21.6+
		1.20	0.22	0.50	1.70	3.99
	Chlorine + Ammonia*	0.99	0.87	0.61	<0.1	2.47
		0.40	0.53	<0.15	<0.1	0.93
		2.60	4.49+	5.68+	1.14+	13.9+
	Ammonia + Chlorine*	0.13	<0.1	<0.1	<0.1	0.13
	Chlorine Dioxide+	0.52	0.71+	<0.1	<0.1	2.62+
1.50	Chlorine	52.0	34.4	24.5	7.0	118.9
		51.9	34.9	24.5	7.0	118.3
	Chlorine + Ammonia*	2.10	2.33	1.63	1.31	7.37
		1.95	1.74	1.48	1.31	6.48
	Ammonia + Chlorine*	0.19	0.10	0.14	<0.1	0.43
		10.5	0.29	<0.1	<0.1	10.8
	Chlorine Dioxide+	0.76	<0.1	<0.1	<0.1	0.76
5.00	Chlorine	95.5	51.7	24.2	8.0	179.2
	Chlorine + Ammonia*	3.06	4.27	1.88	1.03	10.24
	Ammonia + Chlorine*	1.60	1.27	0.55	0.89	4.31
	Chlorine Dioxide	4.16	0.57	<0.1	<0.1	4.73

* Chlorine and ammonia at the same doses
\+ Possible contamination

where: Z = THM concentration, µg/l
R_i = free chlorine residual at end of contact interval, mg/l
t_i = contact interval, sec
M = number of contact intervals
b_o, b_1 = regression coefficients

Application of test system data to the above model yielded equation 18.

$$Z = 0.281 \left(\sum_{i=1}^{M} R_i t_i\right)^{0.466} \qquad (18)$$

The correlation coefficient for 25 data points was 0.815, significant at greater than the 99% level, and the regression coeficient, b_1, was significant at greater than the 99% level. Obviously, use of the preceding model is specific for the test system from which it was derived.

The THM production was also determined for those prototype experiments in which seed organisms were present. No differences were observed in the presence or absence of bacteriological seed. Table 17 shows the TermTHM values obtained in several disinfectant systems. The results included in Table 17 represent several different prototype runs, some of which showed THMFP that varied considerably because of the time of year they were run. Consequently, the TTHM values for a single disinfectant should not be compared directly. However, comparison between disinfectants is feasible for prototype runs performed on same days or with a similar THMFP. The duplicated data for chlorine and chlorine followed by ammonia at doses of 0.5 and 1.5 mg/l illustrates the THM production observed without added seed organism.

Two additional seeding experiments were performed with the prototype system to help ascertain the nature of the THM precursors. Humic acid was introduced in the same manner as with bacteriological or viral experiments into the prototype system at different concentrations and doses of chlorine as the disinfectant. Table 18 and Figure 26 show the THM levels observed from these seeded experiments. The Term THM values were determined by the addition of chlorine to a residual of 0.25 mg/l. The high values observed for the 15 min time point for the 4.2 mg/l humic acid dose are anamalous and may be due to contaminated vials. The second seed experiment involved the addition of chlorophyll-a at relatively low concentration into the prototype system to evaluate its potential as a precursor. Table 19 shows the comparison of levels of THM observed when chlorine is the disinfectant in the presence and absence of the chlorophyll-a seed material. The Term THM values were determined in the presence of a 0.18 mg/l residual.

LABORATORY EXPERIMENTATION

Control experiments involving disinfection of normal water obtained from the Boerne reservoir at several doses of chlorine disinfectant and constant conditions were performed to evaluate the potential of the prototype and the Boerne WTP to produce THM. The chemical parameters for the reservoir water were also measured and found to be identical with values previously described. Table 20 shows selected chemical parameters and Table 21 shows the observed THM production for three doses of chlorine as disinfectant

TABLE 18. Formation of Trihalomethane from Humic Acid Seed of the Prototype System with Chlorine as the Disinfectant

Humic Acid Dose (mg/l)	Sampling Time	Trihalomethanes (µg/l) Chlorine Dose (mg/l) 0.5	1.5	5.0
4.2	0	<0.10	<0.10	<0.10
	1 sec	1.94	1.48	3.51
	31 sec	2.96	5.46	11.7
	72 sec	4.48	5.18	13.1
	15 min	20.3	29.1	32.8
	60 min	15.7	31.5	40.7
	48 hr	13.8	60.4	71.7
	>72 hr	17.06	57.5	410.2
9.2	0	<0.10	<0.10	<0.10
	1 sec	1.54	2.00	8.41
	31 sec	2.53	10.2	16.7
	72 sec	2.60	10.0	21.6
	15 min	11.6	37.9	45.7
	60 min	14.3	49.3	-
	48 hr	12.3	45.6	242.5
	>72 hr	15.1	50.7	352.4

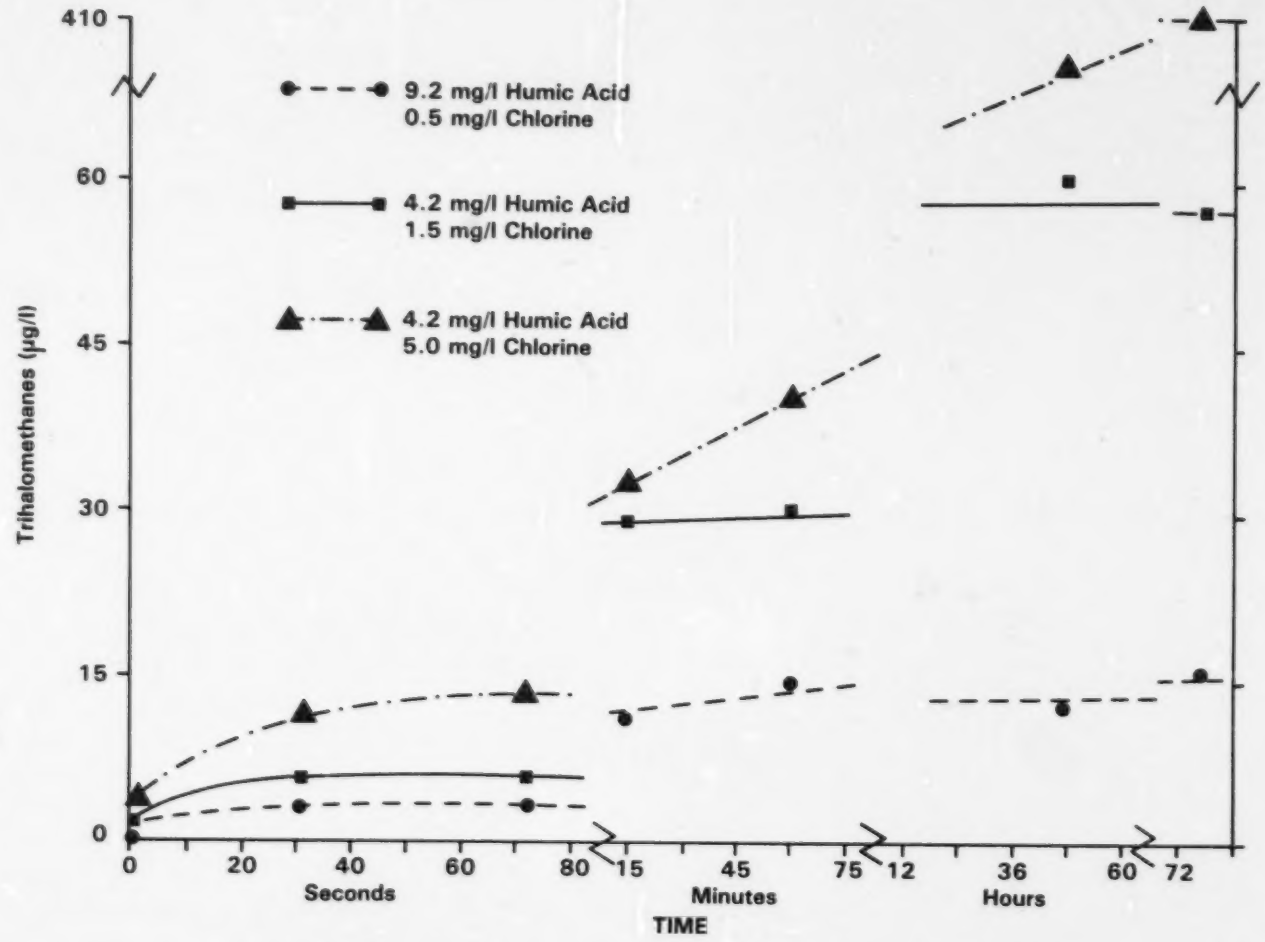


FIGURE 26. Production of Trihalomethanes with Time for Prototype Disinfection with Humic Acid Seed by Chlorine

TABLE 19. Formation of Trihalomethanes from Chlorophyll-a Seed of the Prototype System with Chlorine as Disinfectant

Chlorophyll-a (µg/1)	Sampling Time	Trihalomethanes (µg/1)	
		0.5 mg/1 Cl_2	1.5 mg/1 Cl_2
0.9*	0	<0.10	<0.10
	15 min	2.66	6.43
	60 min	2.28	17.4
	24 hr	2.77	29.5
	48 hr	2.88	25.5
	>72 hr	3.83	32.9
1.9	0	<0.10	<0.10
	15 min	2.94	7.50
	60 min	3.21	18.1
	24 hr	3.35	32.6
	48 hr	3.40	31.7
	>72 hr	4.21	35.2

* Before addition of chlorophyll-a seed (1 µg/1 final concentration in stream)

TABLE 20. Chemical Parameters for Boerne Reservoir Water Under Controlled Disinfection Conditions

Dose (mg/l)	Sampling Time	TOC (mg/l)	Chl-a (µg/l)	Free Cl_2 (mg/l)	Total Cl_2 (mg/l)	pH
0.50	0	4.56 mg/l	2.74	0.45	0.48	8.38
	1 min	3.82	1.56	0.15	0.21	8.26
	15 min	4.62	-	0	0.14	8.36
	1 hr	6.05	1.26	0	0.14	8.37
	12 hr	5.0	-	0	0	8.23
	24 hr	4.48	1.25	0	0	8.20
	48 hr	3.69	-	0	0	8.13
	72 hr	3.61	1.63	0	0	8.13
1.5	0	4.56	2.74	1.35	1.44	8.38
	1 min	3.48	1.12	0.81	0.82	8.06
	15 min	2.89	-	0.53	0.69	8.08
	1 hr	9.26	0.92	0.38	0.52	8.08
	12 hr	2.59	-	0.10	0.38	7.95
	24 hr	3.44	0.92	0	0.11	8.01
	48 hr	3.43	-	0	0	8.07
	72 hr	3.29	1.07	0	0	7.97
5.0	0	4.56	2.74	4.50	4.80	8.38
	1 min	3.07	1.20	4.36	4.71	7.78
	15 min	3.24	-	3.96	4.34	7.80
	1 hr	4.70	0.94	2.65	2.89	7.70
	12 hr	4.95	-	1.91	2.07	7.75
	24 hr	3.98	0.92	1.61	1.84	7.81
	48 hr	4.23	-	1.21	1.44	7.63
	72 hr	4.09	0.96	0.96	1.20	7.76

TABLE 21. Trihalomethane Production from Boerne Reservoir Water Under Controlled Disinfection Conditions

Dose (mg/l)	Sampling Time	Trihalomethanes (µg/l)				
		$CHCl_3$	$BrCl_2CH$	Br_2ClCH	$CHBr_3$	Total
0.50	0	<0.01	<0.01	<0.01	<0.01	0.0
	15 min	2.00	0.66	2.98*	<0.10	5.64*
	1 hr	2.28	<0.10	<0.10	<0.10	2.28
	24 hr	2.05	0.32	<0.10	<0.10	2.37
	72 hr	2.46	0.40	<0.10	<0.10	2.86
	Terminal	2.59	1.24	<0.10	<0.10	3.83
1.50	0	<0.01	<0.01	<0.01	<0.01	<0.01
	15 min	3.83	1.00	1.60	<0.10	6.43
	1 hr	7.78	5.10	4.50	<0.10	17.38
	24 hr	10.74	10.30	8.44	<0.10	29.48
	72 hr	11.99	7.21	6.26	<0.10	25.46
	Terminal	166.58	103.08	38.91	<0.10	299.57
5.00	0	<0.01	<0.01	<0.01	<0.01	<0.01
	15 min	4.92	1.25	<0.10	<0.10	6.17
	1 hr	4.10	5.33	2.84	<0.10	12.07
	12 hr	18.50	12.17	<0.10	<0.10	30.67
	24 hr	36.45	19.44	12.45	<0.10	68.34
	72 hr	49.31	31.18	17.70	<0.12	98.31
	Terminal	254.84	131.02	41.41	<0.10	427.27

* Apparent contamination

measured under controlled conditions (25°C reaction temperature). As data in Table 20 indicates the free chlorine residue was essentially depleted after 15 min for the 0.5 mg/l dose and after 24 hrs for the 1.5 mg/l dose. THM values did not show changes after depletion of the free residual. Term THM values were obtained by chlorine addition to a residual of 0.41, 0.37, and 0.30 mg/l for the 0.5, 1.5, and 5.0 mg/l doses, respectively. The THM value obtained for the 15 min time point of the 0.5 mg/l run was probably artificially high due to a dibromochloromethane value that may have been caused by an interfering substance (or contaminant). Removing that value results in a TTHM of 1.66 µg/l which is in line with the later time points.

To determine the influence of humic materials on the production of THM's a seed experiment with the prototype was performed. Consequently, control reactions using Boerne Reservoir water and distilled water were also performed. The results are shown in Tables 22 and 23. Table 22 depicts the effect of two humic acid doses of 4.2 and 9.2 mg/l on Boerne reservoir water with three doses of chlorine as disinfectant. Higher THM values are observed upon addition of the humic acids to the reservoir water than observed with the humic acids in distilled water (Table 23). A free residual of 0.35 mg/l was maintained for these Term THM values.

Addition of chlorophyll-a to the reservoir water was performed to compare results from the prototype system. Table 24 depicts the relatively small changes observed by addition of chlorophyll-a. Free residuals of 0.27, 0.31, and 0.29 mg/l were maintained for the production of Term THM for the 0.5, 1.5, and 5.0 mg/l runs, respectively.

TABLE 22. Formation of Trihalomethanes from Humic Acid Seeded Reservoir Water with Chlorine as Disinfectant

Humic Acid (mg/l)	Chlorine Dose (mg/l)	Terminal THM (µg/l)
5	0.50	3.89
	1.50	20.02
	5.00	226.4
15	0.50	5.65
	1.50	227.4
	5.00	324.3

TABLE 23. Formation of Trihalomethanes from Humic Acid Seeded Distilled Water with Chlorine as Disinfectant

Humic Acid (mg/1)	Chlorine Dose (mg/1)	Terminal THM (µg/1)
5	0.50	5.15
	1.50	31.98
	5.00	77.03
15	0.50	4.91
	1.50	42.29
	5.00	107.2

TABLE 24. Production of Trihalomethanes from Chlorophyll-a Seeded Reservoir Water with Chlorine as Disinfectant

	Chlorine Dose (mg/1)					
	Chlorophyll-a (µg/1)			Trihalomethanes (µg/1)		
Sampling Time	0.5	1.5	5.0	0.5	1.5	5.0
0	2.74*	2.74*	2.74*	<0.10	<0.10	<0.10
1 min	1.56	1.12	1.20	1.94	3.71	4.03
15 min	-	-	-	2.00	3.83	4.92
1 hr	1.26	0.92	0.94	2.28	7.78	4.10
24 hr	1.25	0.92	0.92	2.05	10.7	36.5
48 hr	-	-	-	1.46	12.0	49.3
>72 hr	1.63	1.07	0.96	2.59	166.6	254.8

* Calculated dose 2.74 µg/1

SECTION 7

DISCUSSION

Analysis of the chemical data for the Boerne Reservoir indicates that the reservoir resembles a young, aligotrophic lake with no significant waste inputs that currently affect water quality. Examination of the present and projected population and land use patterns indicate that no significant industrial or agricultural growth is expected in the water shed and future development would be primarily residential and recreational. Bacteriological data collected also indicate no significant human pollution at this time. Consequently, the THM produced upon chlorination arise only from natural organic material that is delivered to the reservoir by runnoff.

The overall TOC levels observed in the reservoir are low, thus relatively low levels of THM are produced. Depending upon the chlorine dose, a TTHM of 430 µg/l can be observed (Table 21). The data also indicate that humic materials are not the only THM precursors present in the reservoir water since a comparison of control and humic acid seed experiments with a commercial humic acid (Aldrich Chemical Co.) clearly show the level of THM production is three-fold higher for the reservoir plus humic acid than with humic acid alone in distilled, buffered water (Tables 22 and 23). These results are observed regardless of humic acid or chlorine dose employed. An alternative explanation for this three-fold difference would be that the commercial humic material does not resemble the organic material in the reservoir closely enough. Organic material indigenous to the reservoir must be isolated in order to examine this alternative.

Chlorination of reservoir water collected at Site 2 shows a similar trend; however, a complete study was not performed at several chlorine doses and humic acid doses. The TTHM's generated at Site 2 were approximately 40% lower than those observed from the reservoir (Site 1). The difference in TTHM values probably arises from the filtration occurring upon pumping through the rock filled intake. Furthermore, Site 1 is a surface grab sample and contains significant amounts of floating debris.

Comparison of the disinfected reservoir water to the final product produced by the WTP with similar TOC's and chlorine doses shows a 50-60% reduction in TTHM to a range of THM values of 60 - 135 µg/l with an average of 85 µg/l. Coagulation, sedimentation and filtration must remove significant portions of the THM precursors. Comparison of the THM values from the WTP to the humic acid seeded in distilled water (Table 23) exhibit comparable (somewhat lower) THM values. This suggests that the filtration and other processes have removed the majority of materials that contribute to high THM values

upon chlorination of the reservoir water leaving behind soluble humic acid materials that behave similarly to the humic acid seed.

The normal operation of the WTP plant exhibited chemical, bacteriological, and THM values that were essentially identical to those parameters measured during the operation of the prototype system. For example, a typical TTHM of the WTP was 107 µg/l and a TTHM from the prototype (with chlorine disinfection) at approximately the same dose and residual was 118 µg/l. The similarity between systems indicates that the rapid mixing techniques and the addition of a biological seed does not appreciably alter the chemical parameters characteristic of the water.

The effect of the rapid mixing prototype system upon the added bacteriologic seeds (E. coli C, E. coli lys 147 and bacteriophage f_2) was pronounced. Operation of the prototype without introduction of a disinfectant showed that no inactivation of the bacteriologic seed occurred through mechanical effects of the prototype mixer. Consequently, the operation of the rapid mixing prototype system does not alter any of the characteristics of the Boerne water after it has been coagulated and filtered. Since neither the chemical nor the microbiological properties of the water are affected by the rapid hydraulic mixing system, direct application of the results of system operation can be made to normal operation of the Boerne WTP.

Most investigative work concerning rapid mixing and water streams has been directed towards either the role of rapid mixing associated with the addition of a coagulant to optimize floc formation, or the role of rapid mixing associated with the addition of chlorine to enhance the biocidal action of chlorine in a wastewater stream. Longley (1974), working with chlorination of a wastewater stream, achieved excellent bactericidal efficiencies using a plug flow reactor of similar design to the study reactor. He noted, however, that the bactericidal efficiencies achieved in the conventional chlorine contact chamber after the long contact times (approximately 12 - 15 min), approached those achieved with the plug flow reactor.

As demonstrated in Figures 10 - 16, effective disinfection was achieved at low doses of disinfectant due to the efficiency of the tubular plug flow reactor. Stenquist and Kaufman (1972) have cited two reasons for the superiority of a tubular over a backmixed reactor:

1. Backmixing apparently results in a chlorine residual with poorer bactericidal effectiveness because of reaction of the chlorine entering the reactor with residuals previously formed.

2. Shortcircuiting, or the presence in the effluent from the reactor of fluid particles with a very short chlorine contact time relative to the mean contact time, can greatly affect overall performance.

The results of this study support these observations for bacterial inactivation and indicate that a tubular plug flow reactor can be used to advantage to reduce bacterial populations while minimizing THM formation.

The seed organisms utilized in this study were not sufficiently resistant to any disinfection system (with the exception of the chloramines) to provide disinfection curves similar to that generated in static laboratory testing. Clearly, the rapid hydraulic mixing was responsible for the more rapid inactivation since there was no loss of viable organisms due to any mechanical effects of the prototype system. Furthermore, the disinfection of a more resistant viral organism, bacteriophage f_2, convincingly demonstrates the efficacy of the rapid mixing system regardless of disinfectant or microbiological parameter. A simple bivariate model for prediction of SPC organism disinfection efficacy was found to be significant. The model is given by equation 19.

$$y = b_o(Rt)^{b_1} \qquad (19)$$

where: R = disinfectant residual at time zero (mg/l), t = contact time (sec), y = survival fraction of SPC organisms, and b_o, b_1 = regression coefficients

The applicability of this model, and particularly the use of the derived regression coefficients, is questionable in systems where the water quality differs significantly from the water quality of the Boerne WTP at the time the data for the models was derived.

Selleck and coworkers (1978) previously developed a similar model said to describe accurately the inactivation of coliform bacteria with chlorine. This model is given as equation 20.

$$S = (Rt\ /0.0048)^{-1.24} \qquad (20)$$

where: S = bacterial survival ratio (y), R = total chlorine residual at time zero (mg/l), and t = contact time (min).

Rearranging equation 20 into the form used in this study and expressing contact time in sec results in equation 21.

$$S = 0.214\ (Rt)^{-1.24} \qquad (21)$$

When incorporating the regression coefficients found in this study for total chlorine residual, equation 19 becomes equation 22.

$$y = 0.590\ (Rt)^{-0.275} \qquad (22)$$

Clearly, equations 21 and 22 are similar and differ significantly in slope only. The principal explanation for this difference may lie in the fact that equation 22 was developed using indigenous SPC organisms while equation 21 was developed using coliform organisms.

Although coliform bacteria have been used widely in disinfection studies, the behavior of these gram negative organisms as represented by E. coli is significantly different than other bacterial species present in most raw or

inactivated within 15 sec after exposure to all test disinfectants. Similar inactivation kinetics have been observed by others including Roller and associates (1980) who noted a 3.5 $\log_{10}$ reduction of E. coli B within 20 sec after exposure to 2-3 mg/l of chlorine dioxide. The SPC bacteria, on the other hand, comprise a diverse group of organisms which was found to be considerably more resistant to disinfection during this study. LeChevallier and coworkers (1980) determined the composition of the SPC bacterial population in one water system and reported that gram positive organisms were three times more prevalent in chlorinated water than in the raw water source. Their study showed that actinomycetes and Aeromonas species were the two most common groups of SPC bacteria in chlorinated distribution system water and that over 30% of the SPC population could be classified as opportunistic pathogens. Thus, the use of SPC bacteria appears to be more desirable in defining the efficacy of potable water disinfectants.

For those data points where sufficient E. coli lys 147 was available for analysis, a direct comparison can be made between the observed data and calculations of survival ratio by equation 21. As shown in Table 25, equation 21 drastically underestimates the disinfection achieved under the conditions of this study. These results are more impressive when one considers the fact that the E. coli lys 147 was far more sensitive to the disinfectants used under the conditions of this study than was the E. coli C. The explanation for these major differences may lie in the efficiency of the prototype rapid mixing system for disinfection (diffusion) and the differences in test waters.

More recently Selleck and coworkers (1980) have indicated that their model was successfully applied to other disinfectants including chlorine dioxide. As shown in Table 26, where comparable chlorine dioxide data are available equation 21 continued to seriously underestimate the level of disinfection achieved in this study. Further analysis of the data developed in this study suggest that equation 21 more closely approximates the results obtained with the chlorine followed by ammonia and the ammonia followed by chlorine disinfection systems.

Of greater importance was the substantial reduction in THM production observed with the prototype system. As shown in Table 17 lower disinfectant doses produced lower TTHM levels for chlorine. However, there was less of a difference between TTHM formed in the chlorine followed by ammonia system (2.47 µg/l to 10.24 µg/l) than was observed with the chlorine system (6.29 µg/l to 179.2 µg/l) for the same doses. The 15 sec of contact with free chlorine before ammonia addition (CLN) produced higher levels of TTHM when compared to the addition of ammonia followed by chlorine (NCL) at the same dose,but the CLN system demonstrated a bactericidal capability superior to the NCL system. Thus, the ammonia addition was able to prevent additional THM from being produced. This is clearly shown graphically in Figures 27 and 28. Note that disinfection is essentially complete before THM formation increases. The increase in THM from 3 g/l at 1 min to approximately 9 µg/l in the terminal sample was due to slow conversion of intermediates produced by chlorine to THM. Note that only 18% of the THMFP was found in this system.

TABLE 25. Comparison of Experimentally Determined N/N_o for Chlorine and the Calculated Survival Ratio (Selleck et al., 1978)

Chlorine Dose (mg/l)	Contact Time (sec)	N/N_o *E. coli* lys 147	Survival Ratio, S
5.40	1	9.1×10^{-6}	2.6×10^{-2}
1.50	1	$<2.2\times10^{-6}$	7.4×10^{-1}
1.50	15	$<2.2\times10^{-6}$	4.5×10^{-3}
0.50	1	5.8×10^{-2}	5.0×10^{-1}
0.50	1	5.9×10^{-2}	5.0×10^{-1}
0.50	1	5.8×10^{-2}	5.0×10^{-1}
0.50	15	$<3.7\times10^{-6}$	1.7×10^{-2}
0.50	15	$<3.7\times10^{-6}$	1.7×10^{-7}
0.50	15	$<3.7\times10^{-6}$	1.7×10^{-2}
0.45	1	5.3×10^{-2}	5.8×10^{-1}
0.30	15	2.1×10^{-5}	3.3×10^{-2}

TABLE 26. Comparison of Experimentally Determined N/N_o for Chlorine Dioxide and the Calculated Survival Ratio (Selleck et al., 1978).

Chlorine Dioxide Dose (mg/l)	Contact Time (sec)	N/N_o		Survival Ratio, S
		E. coli lys 147	*E. coli* C	
0.55	1	5.8×10^{-2}	6.9×10^{-1}	4.5×10^{-1}
0.55	15	$<2.8\times10^{-6}$	$<5.3\times10^{-7}$	1.6×10^{-2}
0.50	1	5.8×10^{-2}	6.9×10^{-1}	5.0×10^{-1}
0.50	15	$<2.8\times10^{-6}$	$<5.4\times10^{-7}$	1.7×10^{-2}
0.24	15	1.1×10^{-1}	-	1.3×10^{0}
0.24	15	1.1×10^{-5}	-	4.4×10^{-2}

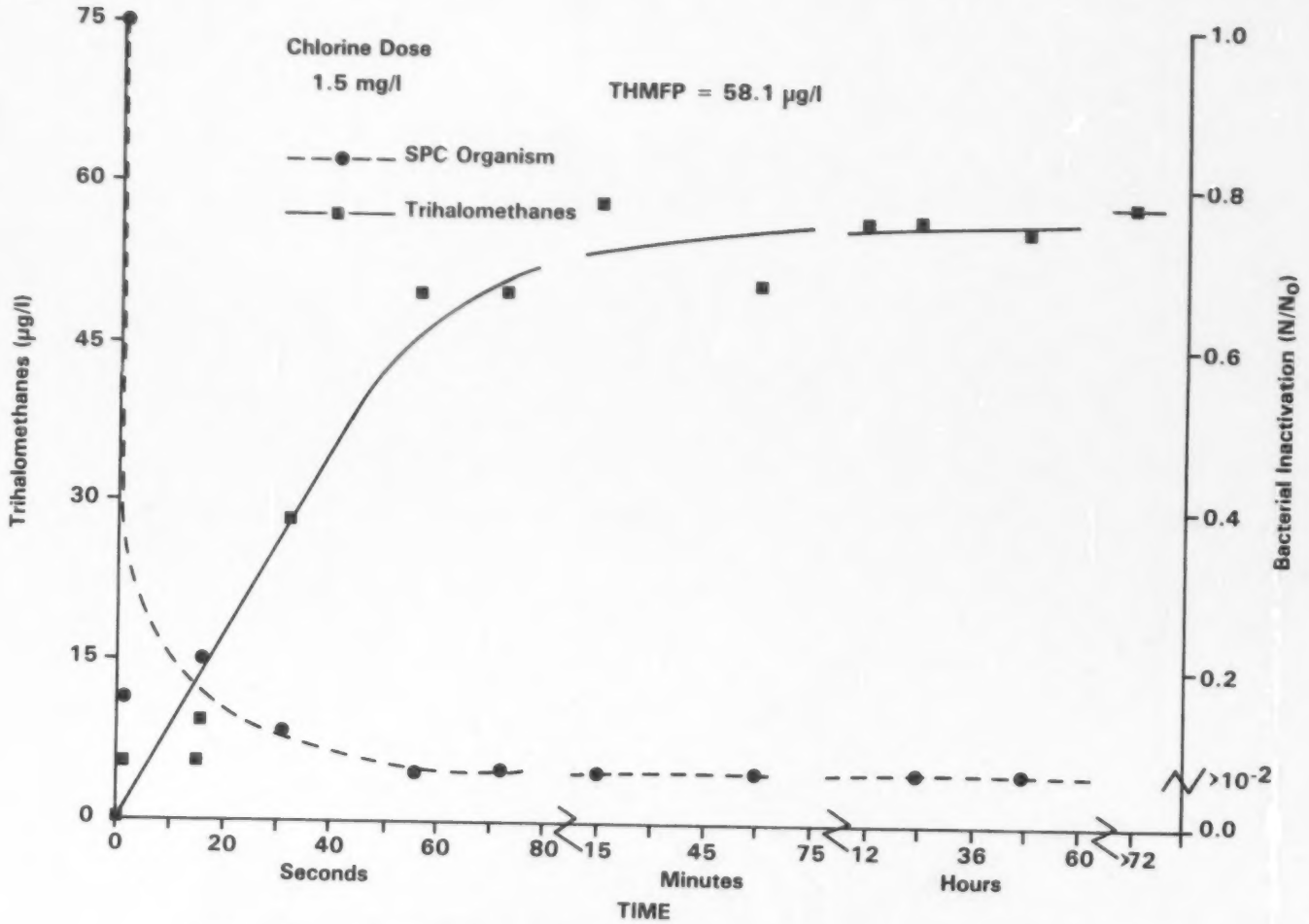


FIGURE 27. Production of Trihalomethanes and Bacterial Inactivation with Time for Prototype Disinfection by a 1.5 mg/l Chlorine Dose

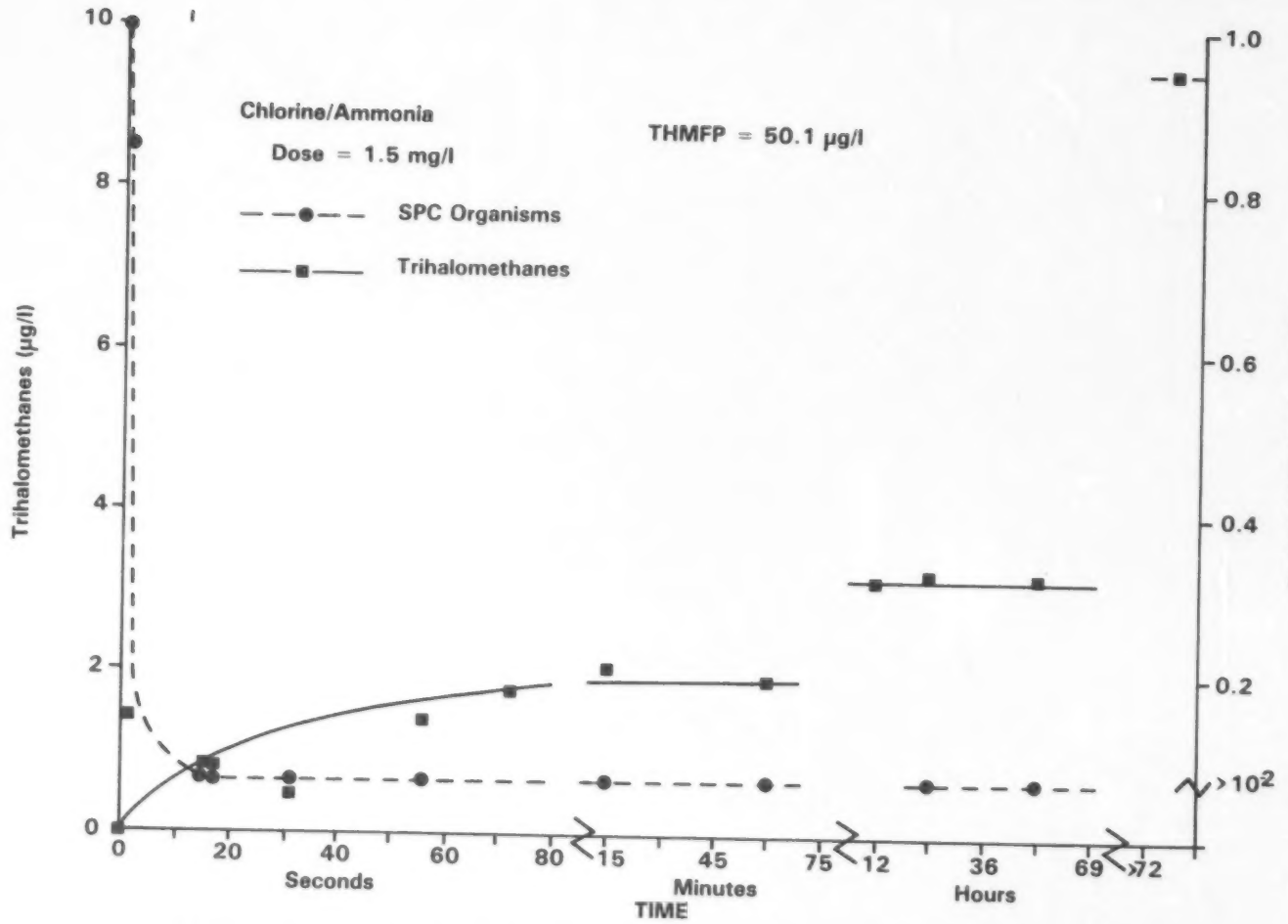


FIGURE 28. Production of Trihalomethanes and Bacterial Inactivation with Time for Prototype Disinfection by a 1.5 mg/l Chlorine Dose Followed by a 1.5 mg/l Ammonia Dose

The two best systems for minimizing THM production were chlorine dioxide and ammonia plus chlorine. The low level THM observed for chlorine dioxide may have been due to low level chlorine contamination in the system produced because of the method of generation of the chlorine dioxide. Significant reduction of THM were observed with chloramine and chlorine dioxide as the disinfectants. A 17 fold reduction in THM production was observed at a 1.5 mg/l dose of chlorine followed by ammonia when compared to the same dose of chlorine and a 275 fold reduction in THM production was observed for ammonia followed by chlorine under the same conditions. Figure 29 depicts the excellent bacterial inactivation and low TTHM levels observed.

Operation of the prototype system was performed with two chemical seeds to determine if the rapid mixing system affects the THM production in a predictable manner. Addition of three doses of humic acid and one dose of chlorophyll-a to the prototype system were accomplished during the study period. Figures 26 and Table 19 show the production of total trihalomethanes with time for the humic acid and and chlorophyll-a seeds, respectively. Both seed systems show increased THM levels over the background indicating that these materials do contribute to the THM production. The smaller increases of THM observed for the chlorophyll-a experiment are consistent with the low level of seed employed. Experiments with humic acid do not exactly parallel either the normal plant operation nor the static laboratory experiments with regard to time course of THM production. The prototype system does appear to affect the THM production. This observation may be explained by the kinetics of the reaction of the disinfectant with the THM precursors. If diffusion of the disinfectant to the organic precursor is rate-controlling, increasing the mixing rate will increase the reaction rate up to a plateau value. However, if the reaction is not controlled by diffusion, the reaction rates will be independent of mixing. For the present system the THM production is slower than observed in other systems. This can be interpreted as a build-up of higher concentrations of intermediate chlorinated compounds by achieving the diffusion plateau. These intermediates then break down more slowly to produce THM because of self-interaction or follow other pathways to materials other than THM. At long disinfectant residence times the levels of THM are comparable between the laboratory and prototype experiments.

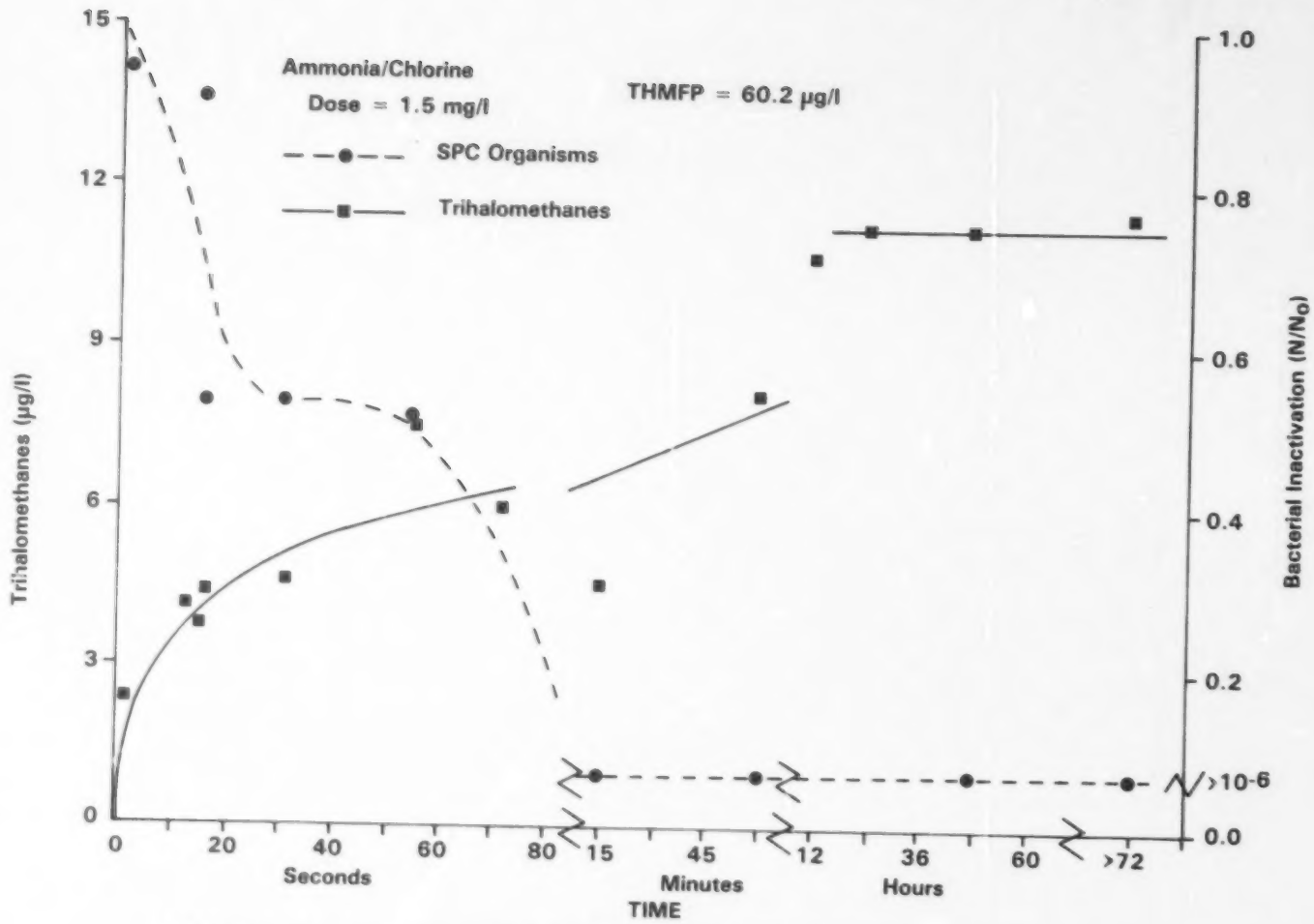


FIGURE 29. Production of Trihalomethanes and Bacterial Inactivation with Time for Prototype Disinfection by a 1.5 mg/l Ammonia Dose Followed by a 1.5 mg/l Chlorine Dose

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